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SOIL SCIENCE

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SOIL SAMPLING WITH A COMPRESSED AIR UNIT

H. F. BLANEY AND C. A. TAYLOR

U. S. Department of Agriculture

Received for publication April 14, 1930

In connection with investigations on rainfall penetration in southern California, the authors[1] are conducting soil moisture studies in which soil samples are taken, at 1-foot intervals to a depth of 18 feet, with the improved soil tube.[2] The success of this work depends, to a considerable extent, upon the speed with which a large number of samples can be obtained, and since the physical effort required may become the limiting factor in obtaining samples at considerable depths, a compressed air unit has been adapted for use in driving the tubes in order that as many samples as desired can be taken quickly and easily.

The apparatus consists of a compressor unit mounted on a truck, a light air hammer, and a 100-foot length of hose. Plate 1 shows the mounting of the apparatus and the manner in which soil tubes are driven. The compressor unit consists of a 2-cylinder air compressor coupled directly to a 4-cylinder gasoline engine with a self-starter, the air receiver and gasoline tank being mounted in front of the compressor. The complete unit is mounted on a channel iron frame and bolted to one side of the truck floor, thus leaving one-half of the truck body space available for carrying other equipment. A reel with 100 feet of ½-inch rubber hose is mounted at the back of the truck and special hose couplings permit connections to be quickly made to the hammer and compressor. An air pressure control automatically maintains any desired pressure up to 150 pounds to the square inch and the displacement of the compressor is 59 cubic feet a minute at 800 revolutions a minute.

The hammer is of the clay digger type, capable, when working under an air pressure of 100 pounds to the square inch, of delivering 2,250 blows a minute, each blow striking with a force of 16 foot-pounds. Extending down into the soil tube is a 6-inch guide rod, the shoulder of which may be seen resting against the end of the soil tube in figure 2 of plate 1. The trigger grip gives the operator ready control of the hammer, and by properly cramping the guide rod in the end of the soil tube, allows very little vibration to be transmitted to the arms of the operator. The jack[3] used for pulling the soil tubes is shown on the ground in figure 1 of plate 1.

[1] Under the supervision of W. W. McLaughlin, Associate chief of the division of agricultural engineering, Bureau of Public Roads, U. S. Department of Agriculture, in coöperation with the State of California, Department of Public Works.

[2] VEIHMEYER, F. J. 1929 An improved soil-sampling tube, *Soil Sci.* 27: 147–152.

[3] TAYLOR, C. A., AND BLANEY, H. F., 1929. An efficient soil tube jack. *Soil Sci.* 27: 351–353.

The set-up for sampling is quickly made, as it is merely necessary to reel the hose out to the desired location and snap it on the compressor. This unit has been in use since October, 1929, and has proved very satisfactory. It is estimated that the time of sampling has been cut to one-third of that required for hand work.

PLATE 1

COMPRESSED AIR UNIT FOR SOIL SAMPLING

FIG. 1. Compressor unit and air hammer in operation.
FIG. 2. Detail view of air hammer.

FIG. 1

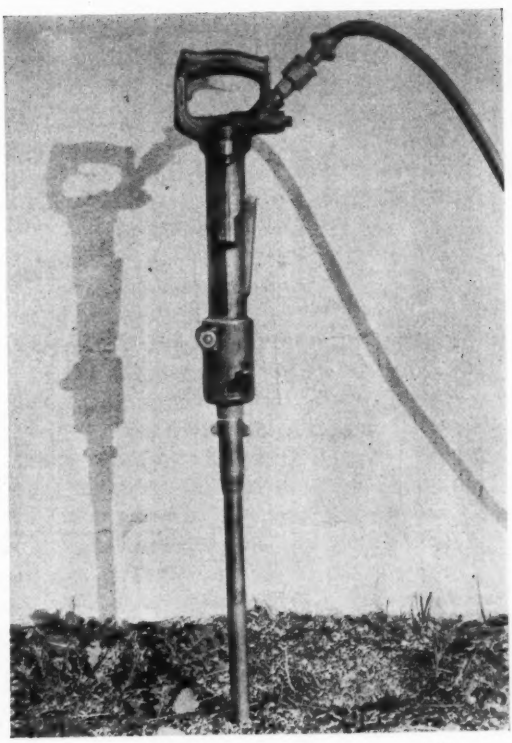

FIG. 2

AMMONIUM CALCIUM BALANCE: A CONCENTRATED FERTILIZER PROBLEM[1]

L. G. WILLIS AND J. R. PILAND[2]

North Carolina Agricultural Experiment Station

Received for publication April 17, 1930

Although much soil fertility research has dealt with the availability and efficiency of the separate ingredients of fertilizers as well as of mixtures, the problem of actual injury to plants resulting from the use of fertilizers has also demanded attention.

In the early development of the fertilizer industry the use of light applications of low grade, low analysis materials required that the major research effort be exerted on the former of these two problems, whereas the recent trend toward more liberal fertilization, and the perfection of chemical processes for the production of fertilizer ingredients of greater solubility and availability has made the latter problem more acute. This is particularly true as it concerns sandy soil types of low absorptive capacity.

Undoubtedly, plasmolysis of plant root tissues is responsible for some of the occurrences of injury consequent to the use of soluble salts as fertilizers, but numerous observations point to other principles governing fertilizer toxicity. As Beaumont (2) points out, the soluble fertilizer materials more highly concentrated in respect to plant nutrients would be less likely to cause injury to plants through plasmolysis than would the cruder salts or those of lower analysis furnishing the same quantity of nutrients. But the same writer (1) reports a reduction in stand of sweet corn and potatoes following the use of high analysis fertilizers in comparison with ordinary materials furnishing equal quantities of nitrogen, phosphorus, and potassium. It was observed, in this case, that the injury, which was limited to the young plants, might be avoided by thoroughly mixing the fertilizer with the soil. The work of Skinner, Williams and Mann (14) has shown a similar injury to cotton seedlings following the use of concentrated fertilizers on Coastal Plain sandy soils, and Skinner (13) has summarized some other observations on this effect of high analysis materials.

Increasing the concentration of nitrogen, phosphorus, and potassium in fertilizers tends to eliminate other elements, and the practicable possibilities in this direction may not be exceeded by mixtures where potassium and ammo-

[1] Publication as no. 41 of the Journal Series authorized by the director of the agricultural experiment station.

[2] Soil chemist and assistant, respectively.

nium are the only cations present. Under such conditions there is the possibility that not only plasmolysis but also the physiological toxicity of these ions may be a factor in fertilizer injury. This type of toxicity, although extensively studied in solution cultures and in relation to alkali soil problems has apparently received little consideration as regards its applicability to fertilization practices.

The physiological toxicity of solutions of single salts is evidenced by abnormal changes in the permeability of the plant cells, or in extreme cases, by disintegration of the tissues. This condition of increased permeability as well as the toxic effects of the solutions of single salts is averted or antagonized by certain salt combinations. In general it has been found that the greatest degree of antagonism exists between salts with monovalent and those with bivalent cations, especially calcium. According to Osterhout (8) this antagonistic effect is due to the presence in the cell of a compound regulating permeability. Toxic and antagonistic salts affect permeability as they accelerate or retard the formation or decomposition of this compound.

Raber (9) explains the phenomenon on the basis of the effect of the electrical charge of the salt on the protoplasm of the cell. The protoplasm being negatively charged, highly positive salts, such as those with bivalent cations, coagulate the protoplasm and thereby decrease permeability, whereas the less positive salts, as typified by those with monovalent cations, increase permeability. Raber's hypothesis, by taking into consideration the electrical properties of the anion as well as the cation, provides an explanation for the variation in the effects of different salts with a common base. The balancing of these electrical effects so as to produce no abnomality in the permeability of the cell is considered the basis of antagonism.

Another theory, that of Hansteen-Cranner (5), is based on evidence of the effect of solutions on the lipoid and pectic materials which govern the peameability of the cell walls. According to this theory the toxic action of the alkalis is due to the dispersion of these components of the cell wall whereas the antagonistic effect of calcum ions results from the coagulative effect of that element.

On strictly thoretical grounds, therefore, the use of fertilizers containing only potassum and ammonium as cations involves the risk of injury to plants. In many cases the rapid absorption of these bases by the soil or an abundant supply of soil calcium would insure safety in the use of such fertilizers, but for soils lacking these features the inclusion of a salt of calcium in the formula might result in a more satisfactory plant response.

Another possible cause of injury to seedling plants may lie in the use of nitrogenous materials easily decomposable in the soil into free ammonia.

Sand cultures containing 10 p.p.m. of nitrogen as free ammonia were found by Russell and Petherbridge (11) to regard the germination of turnip seed whereas with 100 p.p.m. of nitrogen no seed germinated. Since the sand contained 16.7 per cent of moisture it appears that 0.006 per cent of nitrogen as free ammonia is injurious and that 0.06 per cent is fatal.

It is certain, however, that free ammonia would be promptly converted to the

carbonate in any soil; therefore all evidence of the toxicity of free ammonia is in support of the observation of Darwin (3), as quoted by Ehrenberg (4), that ammonium carbonate is injurious to plants.

The possibility of the application of these facts to some concentrated fertilizer problems has been studied by attempting to produce an injury from the use of various materials and to test methods of control based on the foregoing hypotheses.

EXPERIMENTAL

Of the many possible formulas representative of concentrated fertilizers, a mixture of diammonium phosphate, potassium nitrate, and potassium chloride in amounts supplying nitrogen, phosphoric acid, and potash in a 1:2:1 ratio was arbitrarily chosen as representing a practical commercial formula. Ordinary C. P. chemicals were used, being reground when necessary to permit uniform distribution.

A very incoherent Norfolk sand which is being successfully farmed was taken for pot culture experiments and cotton seedlings were used as test plants. The following method of experimentation was used throughout the work:

The soil was wetted to a degree that would insure the germination of the seed without being too wet to be handled. Six and a half pounds of soil was placed into each of enough 1-gallon glazed earthenware pots to provide duplications of the projected treatments. The soil was moderately compacted and the surface levelled.

On this surface, the dry and finely powdered freshly mixed fertilizer materials were distributed as uniformly as possible. Two and a half pounds of soil was added and compacted. Fifteen seeds to each pot were planted with uniform spacing. On this, one pound of soil was spread loosely, and the pots were set to within an inch of their tops in sawdust on a greenhouse bench and covered with waterproof paper. When the seedlings appeared, the paper was removed and distilled water, if necessary, was added uniformly.

As soon as the primary leaves had opened fully, usually in eight or nine days, the soil was washed out of the pots through a screen and the condition of the plants noted. Injury was recorded in those cases where the tap roots of the seedlings had rotted off at the plane of fertilizer application. There was no evidence that germination was in any way affected by the treatments and the percentage of injury is computed from the number of plants having roots extending to or through the fertilizer application.

Toxicity of fertilizer ingredients

The toxicity of the complete fertilizer and of each ingredient and the antagonistic effects of supplementary treatments were tested in duplicate pot experiments.

One and one-half grams to each pot of a mixture containing 0.98 gm. of diammonium phosphate, 0.40 gm. of potassium nitrate, and 0.12 gm. of potassium chloride was used as the basal complete fertilizer. This was approximately equal to a field rate of application of 96 pounds an acre in the drill, of a fertilizer analyzing 17.5 per cent of nitrogen, 35.0 per cent of phosphoric acid, and 17.5 per cent of potash.

At this rate 0.02 of the gram-atomic weight of the combined cations was

supplied to each pot, and each ingredient was tested separately as to toxicity and response to supplementary treatments at the same equivalent concentration as that of the whole formula. Thus, the separate ingredients were used in the following amounts for each pot: diammonium phosphate 1.34 gm., potassium nitrate 2.05 gm., and potassium chloride 1.51 gm.

Supplementary treatments were added in amounts equivalent to one-fifth of the cation concentration of the fertilizer mixture as follows:

	gm.		gm.
Na_2SO_4	.28	$CaSO_4 \cdot 2H_2O$	.69
K_2SO_4	.35	$MgSO_4 \cdot 7H_2O$	.99
NaCl	.23	$CaCl_2 \cdot 2H_2O$	.59
KCl	.30	$MgCl_2 \cdot 6H_2O$	.81

The rate of application of the supplementary treatments was chosen on the basis of observations made in preliminary work on the problem. It does not represent any optimum ratio but only an amount that had been found to establish the effectiveness of the material in controlling toxicity. Differences in solubility and in degrees of ionization of the materials in solution as well as of absorption by the soil would modify considerably the relative concentration of ions to which the seedling plants were exposed. Such differences appear unavoidable and probably do not invalidate the results.

The plan of the experiment and the results are given in table 1.

The data of table 1 demonstrate very strikingly the fact that the complete mixture is toxic to cotton seedlings and that the toxicity is reduced by the addition of calcium chloride but not by sodium or potassium chloride. Apparently magnesium chloride is not quite so efficient in this respect as is the calcium salt but on account of the high degree of variability of the results from duplicate pots minor differences in percentages of injury are of questionable significance. The type of injury and degree of control are illustrated in plate 1, showing the seedlings from duplicate pots on either side of the reference number. None of the supplementary treatments was injurious at the rates of application used.

With the diammonium phosphate, injury was evidenced by the failure of any roots to penetrate below the plane of fertilization. The remedial effect of magnesium salts was almost negligible and that of the calcium salts was distinctly less than when used with the complete mixture. A reasonable explanation of this difference may be found in the fact that the concentration of diammonium phosphate in the mixed fertilizer was less than that of the same component used alone, whereas the concentration of the supplementary treatment was the same for both.

Potassium nitrate was moderately injurious alone and with all supplementary treatments; there was no conclusive evidence of an antagonism similar to that found with the diammonium phosphate. Potassium chloride was non-toxic alone and in all mixtures.

The effectiveness of the calcium and magnesium salts in correcting such toxicity might be acceptable as evidence of simple antagonism of the ammon-

TABLE 1

Injurious effect of a concentrated fertilizer mixture and of the separate ingredients

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	SEEDLINGS INJURED	
				Per pot	Average
				per cent	*per cent*
1	Complete	None	10	100	...
			15	100	100
2	Complete	Sodium chloride	13	100	...
			14	100	100
3	Complete	Potassium chloride	15	100	...
			13	100	100
4	Complete	Calcium chloride	13	16	...
			15	13	15
5	Complete	Magnesium chloride	13	38	...
			14	29	34
6	None	None	13	0	...
			13	0	0
7	None	Sodium sulfate	13	0	...
			10	0	0
8	None	Potassium sulfate	12	0	...
			13	0	0
9	None	Sodium chloride	12	0	...
			13	0	0
10	None	Potassium chloride	14	0	...
			11	0	0
11	None	Calcium sulfate	12	0	...
			11	0	0
12	None	Magnesium sulfate	12	0	...
			13	0	0
13	None	Calcium chloride	14	0	...
			12	0	0
14	None	Magnesium chloride	13	0	...
			13	0	0
15	Diammonium phosphate	None	13	100	...
			12	100	100

TABLE 1—*Continued*

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	SEEDLINGS INJURED	
				Per pot	Average
				per cent	*per cent*
16	Diammonium phosphate	Sodium sulfate	13	100	...
			12	100	100
17	Diammonium phosphate	Potassium sulfate	12	100	...
			8	100	100
18	Diammonium phosphate	Sodium chloride	14	100	...
			13	100	100
19	Diammonium phosphate	Potassium chloride	14	100	...
			14	100	100
20	Diammonium phosphate	Calcium sulfate	13	70	...
			10	50	60
21	Diammonium phosphate	Magnesium sulfate	12	100	...
			11	75	88
22	Diammonium phosphate	Calcium chloride	15	60	...
			10	80	70
23	Diammonium phosphate	Magnesium chloride	12	100	...
			13	75	88
24	Potassium nitrate	None	13	16	...
			14	7	12
25	Potassium nitrate	Sodium sulfate	7	29	...
			13	16	23
26	Potassium nitrate	Potassium sulfate	13	33	...
			12	31	32
27	Potassium nitrate	Sodium chloride	12	9	...
			9	33	21
28	Potassium nitrate	Potassium chloride	13	70	...
			15	13	42
29	Potassium nitrate	Calcium sulfate	13	7	...
			15	0	4
30	Potassium nitrate	Magnesium sulfate	12	25	...
			13	16	21
31	Potassium nitrate	Calcium chloride	11	9	...
			14	43	26

TABLE 1—*Concluded*

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	SEEDLINGS INJURED	
				Per pot	Average
				per cent	*per cent*
32	Potassium nitrate	Magnesium chloride	10	40	...
			12	33	37
33	Potassium chloride	None	12	0	...
			12	0	0
34	Potassium chloride	Sodium sulfate	12	0	...
			12	0	0
35	Potassium chloride	Potassium sulfate	12	0	...
			13	0	0
36	Potassium chloride	Sodium chloride	12	0	...
			12	0	0
37	Potassium chloride	Calcium sulfate	11	0	...
			12	0	0
38	Potassium chloride	Magnesium sulfate	14	0	...
			13	0	0
39	Potassium chloride	Calcium chloride	12	0	...
			10	0	0
40	Potassium chloride	Magnesium chloride	12	8	...
			14	21	15

ium ion if there were no alternate hypotheses suggested by the results of other investigations.

According to Ross, Merz, and Jacob (10), a 1/10 molecular solution of diammonium phosphate has a pH of 8.0 indicating an appreciable degree of hydrolysis with the formation of free ammonia. This is supported by the work of Warren (15), which shows that solid diammonium phosphate has an ammonia vapor pressure of 1.4 mm. at 80°C. The possibility of toxic concentrations of free ammonia being dissociated from the diammonium phosphate in soils of low colloid content is therefore not remote.

On the basis of this hypothesis, it is possible that the protective effect of the added calcium salt might have resulted from a reaction with ammonia, which would be converted to the carbonate by the soil atmosphere, by which the calcium would be precipitated as carbonate and the ammonia remain in solution as the sulfate.

Shive (12) has reported moreover that the phosphate ion is toxic and there

are no good grounds for disregarding the possibility that the beneficial effect of calcium salts may be due to the formation of a relatively insoluble calcium phosphate by reaction with the diammonium phosphate.

As a further complication there is the possibility suggested by the work of Kahlenberg and True (7) and of Hoagland (6) that the hydroxyl ions may be the toxic component.

Toxicity of ammonium salts

In an effort to eliminate as many of these hypotheses as possible, the first step was to determine the toxicity of other salts of ammonia by supplying to each pot equivalent amounts of ammonium from all sources. In this and all subsequent series of pots the basal rate of application was 1 gm. of diammonium phosphate, and the amount of calcium salt used as a supplementary treatment was correspondingly reduced to 0.51 gm. of calcium sulfate or its equivalent.

From the results in table 2 it is distinctly evident that the ammonium ion is not specifically toxic under the conditions of these experiments, but the injury with the monoammonium phosphate rather supports the idea that the phosphate ion or the ammonium combined as phosphate may be moderately toxic. The severity, however, is very much less than that experienced with the diammonium phosphate and it may be that doubling the rate of application of the phosphate ion to maintain the ammonium concentration constant has in this case aggravated a cause of toxicity of minor importance. This assumption is supported by the observation that, with the corrective effect of calcium sulfate, the diammonium phosphate was the less injurious.

The toxicity of phosphates

If the injury from the diammonium phosphate were due to the toxicity of the phosphate ion and the remedial effect of calcium salts were a result of decrease in the phosphate-ion concentration, no benefit should be noted from the use of calcium phosphate as a supplementary treatment. The result of a test of monocalcium phosphate in this capacity is given in table 3, calcium sulfate being included for comparison. Both calcium salts were used in chemically equivalent amounts.

Although the calcium phosphate is not so efficient a corrective of toxicity as is the sulfate it did produce a distinct favorable response. It is obvious from this result that the remedial effect of the calcium salt cannot be due to a reduction of the concentration of toxic phosphate ions and, by inference, it appears doubtful that the toxicity of diammonium phosphate can be due entirely to the high concentration of phosphate.

Some consideration has been given to the possibility that diammonium phosphate is toxic because of the liberation of free ammonia by reaction of the salt with the soil. This could be expected if the phosphate ion were more rapidly absorbed than the ammonium ion. The failure of several attempts to show significant differences in the rates of absorption of these two ions does not, however, offer much support for such a hypothesis.

TABLE 2

Toxicity of ammonium salts

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	INJURY TO SEEDLINGS	
				Per pot	Average
				per cent	*per cent*
1	Diammonium phosphate	None	9	100	...
			14	100	100
2	Diammonium phosphate	Calcium sulfate	13	15	...
			15	27	21
3	Monoammonium phosphate	None	13	62	...
			15	62	62
4	Monoammonium phosphate	Calcium sulfate	13	54	...
			12	33	44
5	Ammonium nitrate	None	11	0	...
			13	0	0
6	Ammonium nitrate	Calcium sulfate	14	0	...
			10	0	0
7	Ammonium sulfate	None	12	0	...
			13	0	0
8	Ammonium sulfate	Calcium sulfate	15	0	...
			14	0	0
9	Ammonium chloride	None	11	0	...
			13	0	0
10	Ammonium chloride	Calcium sulfate	13	0	...
			14	0	0

TABLE 3

Antagonism between diammonium phosphate and monocalcium phosphate

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	SEEDLINGS INJURED	
				Per pot	Average
				per cent	*per cent*
1	Diammonium phosphate	None	9	100	...
			14	100	100
2	Diammonium phosphate	Monocalcium phosphate	14	62	...
			13	62	62
3	Diammonium phosphate	Calcium sulfate	13	15	...
			15	27	21

Free ammonia as the toxic component

The remaining hypotheses, that the hydroxyl ion or that free ammonia might be the toxic factors, were investigated through the use of calcium carbonate as a supplementary treatment at a rate equivalent to the applications of calcium sulfate. The carbonate should not greatly modify the hydroxyl-ion concentration of the solution of diammonium phosphate nor would it neutralize any free ammonia. On the other hand, because of its comparative insolubility it might be ineffective or by the liberation of free ammonia it might increase the toxicity. To cover this latter contingency, the effect of calcium carbonate and calcium sulfate on the toxicity of ammonium hydroxide was also studied. Ammonium hydroxide was distributed in 10 ml. of solution at a rate equivalent to one-half of the total ammonium content of 1 gm. of diammonium phosphate. This ratio was adopted to provide as nearly as possible a quantity of free ammonia comparable with that of the hydrolyzable secondary ammonium radical of the diammonium phosphate.

There are numerous limitations to such a comparison. The initial concentration of free ammonia added as hydroxide would be much greater than the equilibrium concentration of free ammonia derived from the diammonium phosphate. In contact with the soil, however, the concentration of free ammonia from the added hydroxide would rapidly be reduced by adsorption whereas that produced by the hydrolysis of the phosphate should be more nearly constant. Another indeterminate factor is the effect of carbonation of the free ammonia from both sources by contact with the soil atmosphere. The limitations imposed by these variable factors do not, however, entirely preclude a comparison of these two materials and the remedial effect of calcium compounds.

The failure of the calcium carbonate to correct the injury from the diammonium phosphate (table 4) does not controvert the fundamental property of calcium in this respect because of the possibility already suggested that the calcium carbonate might increase the concentration of free ammonia without correspondingly increasing the concentration of calcium available for antagonism.

The similarity in the degree of injury from ammonium hydroxide and from diammonium phosphate does not prove that the causes are qualitatively alike although the effectiveness of calcium sulfate as a corrective of the ammonium hydroxide toxicity gives strong support to that conclusion. The slight but probably significant decrease in the extent of injury from ammonium hydroxide when supplemented by calcium carbonate eliminates the probability that a reduction in the concentration of hydroxyl ions was the sole cause of the previously noted remedial effect of the calcium salts (plate 3).

This result with calcium carbonate and ammonium hydroxide strongly indicates that the calcium has a direct physiological effect independent of any chemical reaction in the medium. There is the possibility however that the greater efficiency of the sulfate is not due entirely to a more intensive antagon-

ism but to an additive effect of a chemical reaction, probably the formation of the non-toxic ammonium sulfate.

In practice, fertilization with diammonium phosphate or other materials productive of free ammonia may not be injurious on highly absorptive soils or when the fertilizer is applied long enough in advance of planting to provide for complete absorption. Under other conditions, the use of gypsum as a supplement may constitute an effective means of control. Ground limestone will probably not serve the same purpose.

This type of fertilizer injury constitutes a problem only with germinating and seedling plants and it is probable that the ultimate effect on the crop would depend on the nature of the rooting systems of the plants fertilized. Taprooted

TABLE 4

The effect of calcium carbonate on free ammonia injury

TREATMENT NUMBER	FERTILIZATION	SUPPLEMENT	NUMBER OF SEEDLINGS	INJURY TO SEEDLINGS	
				Per pot	Average
				per cent	*per cent*
1	Diammonium phosphate	None	15	100	...
			13	100	100
2	Diammonium phosphate	Calcium carbonate	9	90	...
			11	100	95
3	Ammonium hydroxide	None	12	100	...
			14	93	97
4	Ammonium hydroxide	Calcium sulfate	11	36	...
			13	69	51
5	Ammonium hydroxide	Calcium carbonate	9	77	...
			14	78	78

plants would naturally be most subject to damage but this might be corrected by the later development of lateral roots.

Although the method of use of the fertilizer would also govern the probability of injury it would seem best to correct as far as possible all of the toxic properties that are recognized, leaving the placement of the fertilizer to control only the otherwise unavoidable causes of injury.

SUMMARY

In a pot culture experiment with a sandy soil of low absorptive capacity a mixture of C. P. diammonium phosphate, potassium nitrate, and potassium chloride was toxic to cotton seedlings. The cause of injury was related to some property of the diammonium phosphate. The rate of application of the mix-

ture was equivalent to 96 pounds to the acre, in the drill, of a fertilizer analyzing 17.5 per cent nitrogen, 35 per cent phosphoric acid, and 17.5 per cent potash.

The free ammonia formed by the hydrolysis of diammonium phosphate was apparently the most toxic component.

No injury was observed from the use of ammonium as the sulfate, chloride, or nitrate, nor did the alkalinity of the diammonium phosphate appear to contribute to the injurious effect.

Calcium salts were antagonistic to ammonia toxicity, calcium sulfate and chloride being more effective in this regard than calcium carbonate and phosphate. Magnesium salts exhibited the same effect but they functioned less efficiently than did the corresponding calcium salts.

The conversion of free ammonia to carbonate in the soil and its partial neutralization by reaction with the calcium salts could account for the greater part of the beneficial effect of the calcium salts but there was some evidence that physiological antagonism was also a factor. It is not impossible that both of these may contribute to the favorable result.

Monoammonium phosphate alone produced a lesser degree of injury than did diammonium phosphate. This relation was reversed when both were supplemented by admixture with calcium sulfate.

The practical possibilities of gypsum as a supplement to all fertilizers or other soil treatments supplying free ammonia to soils in toxic concentrations is indicated by the work.

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PLATE 1

TYPE OF INJURY TO COTTON SEEDLINGS AND DEGREE OF CONTROL AS A RESULT OF COMPLETE FERTILIZER SUPPLEMENTED WITH OTHER TREATMENTS

In this plate and in plates 2 and 3, all the germinated seedlings from each of duplicate pots are shown on either side of the reference number. The dark line indicates the plane of fertilizer application.

FIG. 1. Complete fertilizer treatment no. 1 (table 1).

	gm.
Diammonium phosphate	0.98
Potassium nitrate	0.40
Potassium chloride	0.12

FIG. 2. Complete fertilizer treatment no. 4 (table 1).

	gm.
Complete fertilizer	1.5
Calcium chloride	0.59

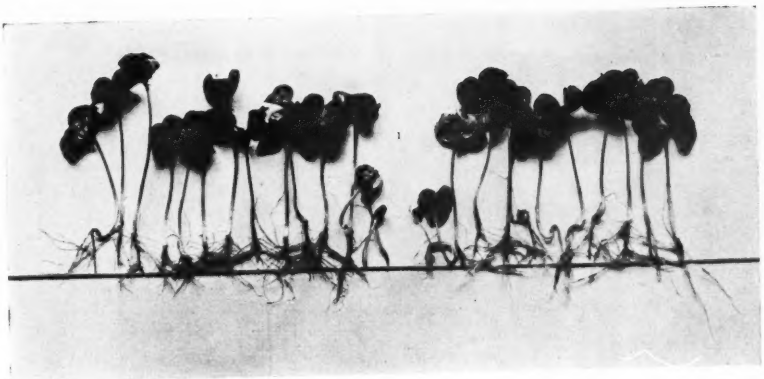

FIG. 1

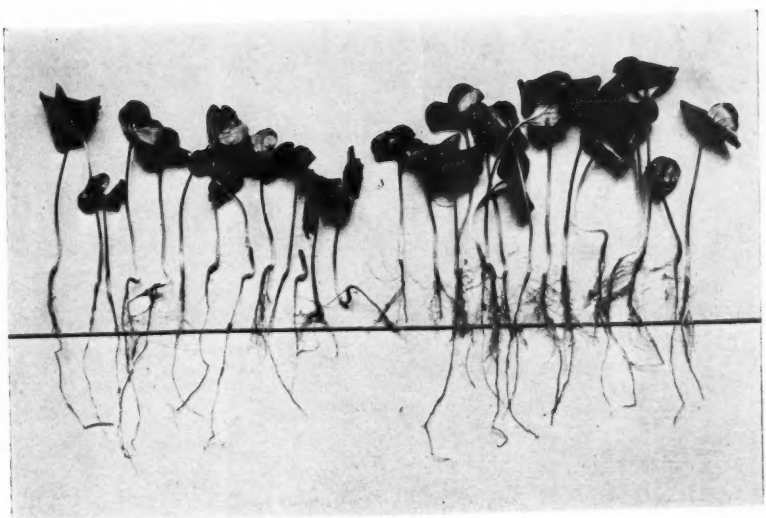

FIG. 2

PLATE 2

EFFECT OF DIAMMONIUM PHOSPHATE ON GROWTH OF COTTON SEEDLINGS

FIG. 1. Diammonium phosphate (1 gm.) treatment no. 1 (table 3).

FIG. 2. Diammonium phosphate treatment no. 3 (table 3).

	gm.
Diammonium phosphate	1
Calcium sulfate	0.51

FIG. 3. Diammonium phosphate treatment no. 2 (table 3).

	gm.
Diammonium phosphate	1
Monocalcium phosphate	0.75

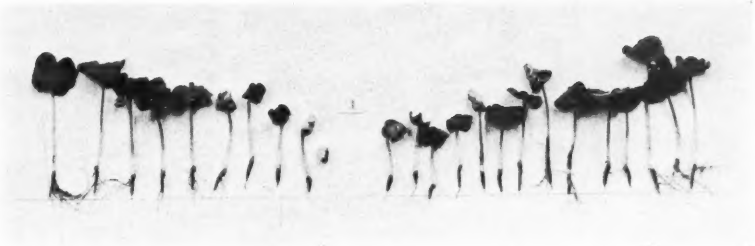

FIG. 1

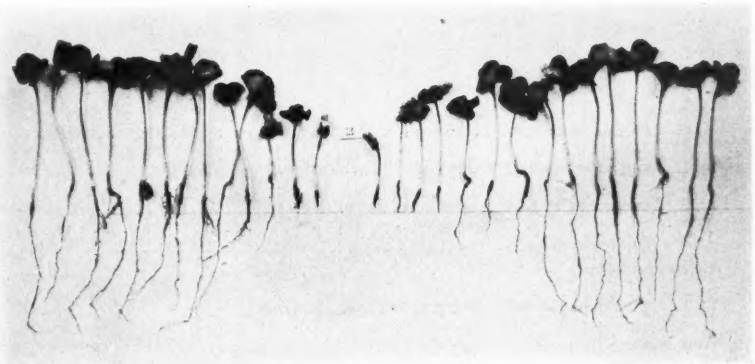

FIG. 2

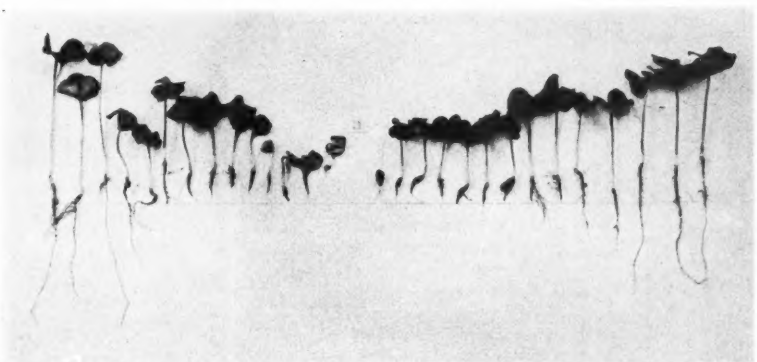

FIG. 3

PLATE 3

EFFECT OF CALCIUM SALTS ON AMMONIUM HYDROXIDE INJURY TO COTTON SEEDLING

FIG. 1. Ammonium hydroxide (0.13 gm.) treatment no. 3 (table 4).

FIG. 2. Ammonium hydroxide treatment no. 4 (table 4).

	gm.
Ammonium hydroxide	0.13
Calcium sulfate	0.51

FIG. 3. Ammonium hydroxide treatment no. 5 (table 4).

	gm.
Ammonium hydroxide	0.13
Calcium carbonate	0.29

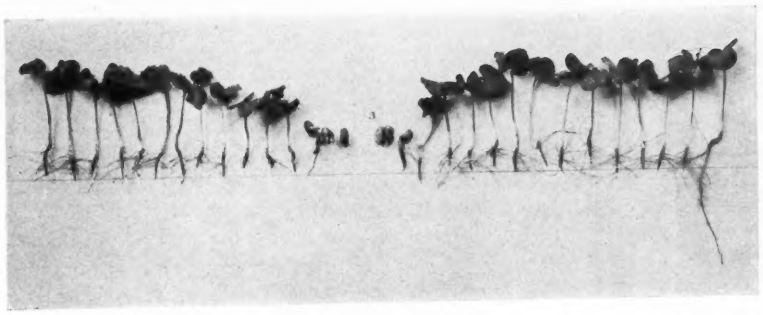

FIG. 1

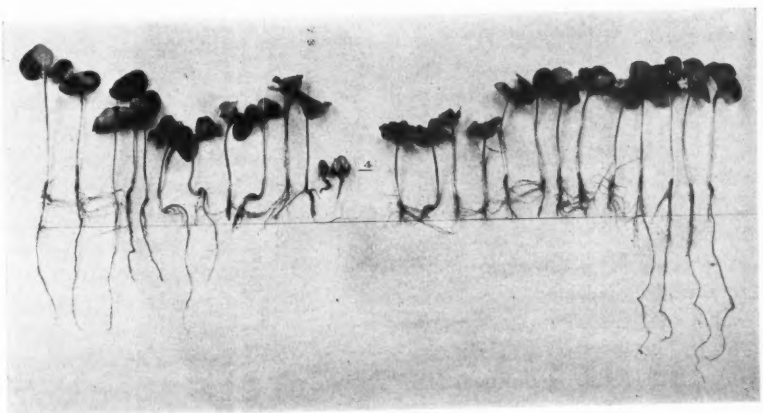

FIG. 2

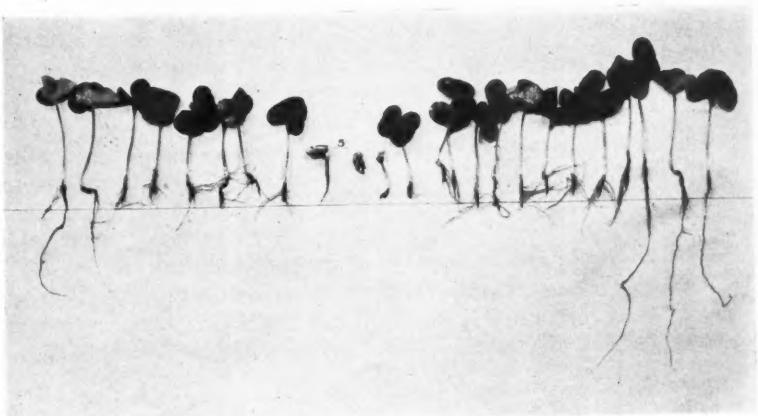

FIG. 3

THE NATURE OF THE BASE-EXCHANGE MATERIAL OF BENTONITE, SOILS, AND ZEOLITES, AS REVEALED BY CHEMICAL INVESTIGATION AND X-RAY ANALYSIS

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It is well established that the replacement of one cation by another produces significant changes in the chemical, physical, and plant nutritional properties of the soil. Various investigators have recognized that soils vary in their content of replaceable cations. "Base-exchange capacity" is the term employed by many soil investigators to denote the total content of all exchangeable cations. Hissink's *T* value represents a similar conception.

J. T. Way concluded in 1852 that the base-exchange substances of soils are of two kinds, namely, organic and inorganic. The discussion presented in this paper is concerned entirely with the inorganic constituents. Way suggested that the inorganic base-exchange constituents of soils belong to the alumino silicates, and that they are analogous to the zeolites. This view is still held by many soil investigators both in Europe and in America. On the other hand, Van Bemmelen concluded more than 40 years ago that the replaceable bases are held by the soil not as ordinary chemical compounds, but that they are adsorbed on the surface of the colloidal particles of the soil. The adsorption hypothesis, with perhaps slight modification, is still held by many European investigators. The term "adsorption compounds" is often used to denote the base-exchange material of the soil.

In connection with the study of the base-exchange property of soils, we have devoted considerable attention to a natural clay known as bentonite. It is now well established that this clay is remarkably similar to the soil in so far as its base-exchange property is concerned. By subjecting the crude clay material to the process of sedimentation, it is possible to separate the base-exchange substance from most of the various impurities which are commonly associated with it.

Many of the bentonitic clays are highly colloidal and possess pronounced base-exchange power. Ross and Shannon (5) have shown that the dominant and most important constituent of certain types of bentonite is the micaceous crystalline mineral, montmorillonite. As is well known by colloid chemists,

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the fact that a given material is crystalline does not preclude its being colloidal, for there are many known examples of crystalline materials which possess pronounced colloidal properties. As used by chemists the term "colloidal" refers primarily to the size of the particles and the fact that the particles will remain in suspension more or less indefinitely, and not to the shape, atomic structure, or the chemical composition of the particles. Obviously, if a colloidal material is crystalline, the individual crystals must necessarily be extremely small. Wherry (7) has suggested that the tabular crystals of bentonitic clays are microscopic in breadth but of colloidal thickness.

As stated already the bentonitic clays possess pronounced base-exchange property. We have found, however, that the purified substances separated from the crude clays of different sources, differ both in their total content of replaceable bases and in the relative ratios of different replaceable bases. All of the bentonites that we have studied contain more or less replaceable magnesium. The deposits which occur in certain localities contain considerable replaceable calcium. Other samples contain much replaceable sodium. We have examined one sample which contains considerable replaceable potassium. All of these bentonites contain much magnesium, and one of them considerable potassium, that are not replaceable by ordinary methods. On the other hand, practically all of the calcium and sodium are replaceable.

EFFECT OF GRINDING

Three of the purified bentonites which we have studied were found to be remarkably similar, having, as shown in table 1, a base-exchange capacity of 105 to 110 milliequivalents to every 100 gm. of air-dry material. The base-exchange capacity of the purified bentonites obtained from other sources ranged from 82 to 88 milliequivalents to every 100 gm., whereas still other samples contain about 55 milliequivalents of replaceable bases. Since one type of bentonite that was employed in our investigation was known to contain the crystalline mineral, montmorillonite, it was decided to study the effects produced by grinding these materials in a ball mill.

In the first experiment a sample of calcium-saturated bentonite, containing 106 milliequivalents of replaceable calcium, was placed in a ball mill and ground for several hours. The material was then subjected to a determination of the replaceable bases. The results showed that the grinding process materially increased the replaceable magnesium, but did not appreciably affect the replaceability of other elements. As is shown in table 2, grinding for 72 hours brought about a very marked increase in the replaceable magnesium.

The bowl of the ball mill used in this investigation was porcelain lined and the balls were composed of high-carbon-chromesteel, $\frac{3}{8}$ inch and $\frac{1}{2}$ inch in diameter. The flint pebbles, commonly employed in ball mill grinding, are not satisfactory for this type of experiment, because they undergo abrasion to such an extent as substantially to contaminate the experimental material. We have not attempted to determine the most efficient method of grinding these

materials. All of the samples were air dried. It was noted that the colloidal materials tended to cake on the walls of the ball mill and the surface of the balls. It is probable that the particles of colloids of this type will be more effectively ground if the sample is partially dehydrated. In other experiments some indication was found that grinding affects the Ca-saturated material to a greater extent than the Na-saturated form. This is probably due to differences in absorbed water.

As has been stated, the sample used in the first experiment was approximately calcium saturated before being subjected to grinding. The calcium

TABLE 1

*Replaceable bases of bentonites**

LABORATORY NUMBER	LOCALITY	MILLIEQUIVALENTS PER 100 GM.				
		Ca	Mg.	K	[Na	Total
1	Death Valley, California	32	34	7	33	106
2	San Diego, California	34	54	4	18	110
3	Osage, Wyoming	7	8	5	66	86
4	Merritt, British Columbia	36	15	3	4	58
5	Rosedale, Alberta	26	11	5	46	88
6	Princeton, British Columbia	45	8	0	0	53
7	Goldfield, Nevada	27	28	6	44	105
8	Medicine Bow, Wyoming	18	20	4	40	82

* The analyses were made on products separated from the crude bentonites by the process of repeated sedimentation in alcohol.

TABLE 2

Effect of grinding bentonite No. 7

	MILLIEQUIVALENTS REPLACEABLE BASES				
	Ca	Mg	K	Na	Total
Unground sample*	106	0	0	0	106
Ground 30 hours	107	68	Trace	Trace	175
Ground 72 hours	106	222	Trace	Trace	328

* This sample was saturated with calcium before the experiments were made.

saturation was effected by prolonged leaching with a neutral solution of normal calcium chloride, the occluded calcium chloride being then removed by leaching with water. After being thus saturated with calcium the sample contained 4.60 per cent total MgO, which, as stated already, was non-replaceable before grinding. After the sample had been ground for 72 hours, a high percentage of the total magnesium was replaceable. If the sample is ground sufficiently thoroughly, probably all of the magnesium will be replaceable.

Bentonites from other sources were also investigated. One of these, bentonite no. 2, was saturated with calcium before it was subjected to grinding.

The other sample, no. 3, was separated by sedimentation in methyl alcohol. The material thus obtained contained the replaceable bases originally present in the crude clay. The results are shown in table 3. It will be noted that grinding produced much the same effect with bentonite no. 2 as with bentonite no. 7, reported in table 2. On the other hand, bentonite no. 3 was affected to a lesser degree. The chief replaceable base of this last named sample, before it was ground, was sodium, and its total content of all replaceable bases was approximately 85 milliequivalents to every 100 gm. It will be noted that again the only base whose replaceability was affected by the grinding was magnesium.

Grinding experiments were also made with a sample of the calcium-saturated material separated from the so-called potash bentonite (5), and a similar experiment was made on a sample of beidellite. According to Ross and Shannon, beidellite belongs to the bentonitic clays and is related to the montmorillonite bentonites. The results are reported in table 4.

TABLE 3

*Effect of grinding bentonites**

	MILLIEQUIVALENTS REPLACEABLE BASES				
	Ca	Mg	K	Na	Total
Bentonite no. 2, unground	108.0	0	0	0	108.0
Bentonite no. 2, ground 72 hours	106.0	220.5	Trace	Trace	326.5
Bentonite no. 3, unground	6.6	12.6	3.7	61.7	84.6
Bentonite no. 3, ground 24 hours	7.8	44.1	4.1	65.3	121.3

* Bentonite no. 2 was saturated with calcium before the experiments were made. Untreated bentonite no. 3 was used.

It will be noted that before these materials were ground their total replaceable base content was considerably less than that of the bentonites already discussed. Grinding, however, produced marked effects on the replaceable-base content. In the case of the potash bentonite the replaceable magnesium and potassium were both markedly increased. The replaceable potassium of the beidellite was also increased to a considerable extent. The magnesium, however, was affected to a still greater extent. On the other hand, the replaceable calcium and sodium were but slightly affected by the grinding.

Effect of grinding soil colloids

The marked effects on the replaceable bases produced by grinding the colloidal samples of bentonite and beidellite suggested similar experiments with soil colloids. The method used in separating the colloidal material from the soil mass was essentially as follows: Several hundred grams of air-dry soil was leached with a solution of sodium chloride in order to replace the natural bases with sodium and thus facilitate the dispersion of the colloidal material. The soil

was then suspended in a relatively large volume of water, and the material remaining in suspension after standing 24 hours was syphoned off. The residue was again shaken with water and the process of sedimentation and syphoning was repeated several times. The colloidal suspensions thus obtained were coagulated with calcium chloride and re-treated several times with fresh solutions of calcium chloride. After the excess of calcium chloride was leached out with distilled water the organic constituents were removed, either by direct oxidation with hydrogen peroxide, or by first extracting with 4 per cent ammonia and then oxidizing with hydrogen peroxide. When the organic constituents had been removed, as was indicated by a carbon determination, the inorganic colloidal material was thoroughly leached with normal calcium acetate in order to effect complete calcium saturation. The soluble calcium salt was leached out with methyl alcohol and the sample was dried at a low temperature. The material was then reduced to a fine powder by careful crushing in a hand mortar.

TABLE 4

*Effect of grinding potash bentonite and beidellite**

	MILLIEQUIVALENTS REPLACEABLE BASES				
	Ca	Mg	K	Na	Total
Potash bentonite, unground	31.8	2.0	0.9	0	34.7
Potash bentonite, ground 30 hours	32.3	38.4	29.0	2.3	102.0
Beidellite, unground	47.0	4.2	Trace	Trace	51.2
Beidellite, ground 3 days	55.0	59.0	18.7	1.7	134.4

* These minerals were obtained from C. S. Ross of the U. S. Geological Survey. The samples were saturated with calcium before being ground.

Five different soil colloids were investigated by the grinding method. The results are recorded in table 5. It will be noted that the effect of grinding these soil colloids was remarkably similar to that produced on the bentonites. The replaceable bases of soil colloid no. 7083, which was separated from a California soil, were most markedly affected, the total replaceable base content being increased from approximately 65 milliequivalents to 205 milliequivalents. It will be noted that with this soil colloid magnesium was the chief base whose replaceability was affected, more than 100 milliequivalents of magnesium having been made replaceable as a result of grinding. Approximately 29 milliequivalents of potassium were also made replaceable. Another soil colloid from California, no. 431, was also markedly affected by grinding, and in this case magnesium was again the chief base whose replaceability was increased. The replaceability of the potassium was also affected, but to a smaller degree than that of magnesium. The replaceability of calcium was not materially affected by grinding either of these soil colloids.

Similar results were obtained with colloids 3232 and 7680. The former was

separated from a glacial drift soil of Indiana and the latter from a limestone soil of central Tennessee. It will be noted that the effect of grinding was less marked with these samples than with the soil colloids from the semiarid region of California, but again the elements that were most markedly affected were magnesium and potassium. With these samples grinding also produced very little effect upon the replaceability of the calcium. The colloid from a highly acid soil of the Cecil series is especially interesting in that the effect of grinding was most marked with the H ion. The calcium-saturated form of this colloid was approximately neutral, but, after being ground, its pH was found to be 5.8. It then contained 60 milliequivalents of replaceable H ions. With this soil colloid the bases whose replaceabilities were increased to the greatest extent by grinding were again magnesium and potassium, but the increases were less marked than in the case of the previously mentioned soil colloids.

Tables 2, 3, 4, and 5, indicate that the soil colloids are remarkably similar to the bentonitic clays, in so far as the effect of grinding is concerned. With the soil colloids from California, 431 and 7083, magnesium was the base most markedly affected, whereas the effect of grinding the colloids from the soils of the more humid parts of the United States was distributed approximately equally between magnesium and potassium. In no case was the replaceability of calcium markedly affected by grinding.

It will be noted that the total content of replaceable bases held by the unground samples of soil colloids 431, 7083, 3232, and 7680, is of the same general magnitude as that of the bentonites 4 and 6, potash bentonite, and beidellite. Moreover, grinding increased the content of replaceable bases of these materials similarly.

The total bases of these soil colloids are reported in table 6. The data are expressed as milliequivalents for each 100 gm. for convenience of comparison with the replaceable bases. It will be seen that, with the exception of colloid 7680, practically all of the calcium contained by these soil colloids is replaceable. Total analyses of the bentonites showed that practically all of their calcium is also replaceable. It will be noted that although the potassium in the unground samples of these soil colloids was not replaceable practically all of it was made replaceable by grinding. The same is true as regards the magnesium of soil colloid 431. On the other hand, much of the magnesium in the other soil colloids still remained in a non-replaceable form after they had been subjected to grinding for the periods employed in these experiments. In view of the result obtained by grinding the sample of bentonite for different periods of time, it is possible that more drastic grinding of the soil colloids would bring about a still further increase in the replaceable magnesium. All of these soil colloids were quite low in total sodium.

Thus it is shown that the chief effect of grinding these soil colloids was, first, to increase the replaceability of their magnesium to a marked extent, and, secondly, to render the potassium replaceable. The results are, therefore, markedly similar to those obtained with the bentonites. The preceding results

strongly suggest that the base-exchange constituents of both the soil colloids and the highly colloidal bentonites are crystalline and that the replaceable bases are contained within the interior of the crystals as well as on the exterior.

X-RAY INVESTIGATIONS

In order to obtain further information concerning the nature of the base-exchange materials, we have made studies on a number of samples of bentonites and soil colloids by the method of X-ray crystal analysis.

TABLE 5

*Effect of grinding soil colloids**

	MILLIEQUIVALENTS REPLACEABLE BASES				
	Ca	Mg	K	Na	Total
Soil colloid 7083, unground	58.1	6.1	0.3	1.1	65.6
Soil colloid 7083, ground 30 hours	60.4	109.3	29.0	5.4	204.9
Soil colloid 431, unground	54.7	2.5	0	0	57.2
Soil colloid 431, ground 30 hours	59.9	71.2	25.3	0	156.4
Soil colloid 3232, unground	54.0	2.7	1.0	1.4	59.1
Soil colloid 3232, ground 72 hours	57.3	21.0	19.3	13.6	111.2
Soil colloid 7680, unground	32.8	2.3	0	1.0	36.1
Soil colloid 7680, ground 30 hours	41.7	27.3	26.0	0	95.0
Soil colloid 11954, unground	14.2	0	0.2	3.9	18.3
Soil colloid 11954, ground 30 hours	14.0	6.8	7.3	6.0	34.1

*No. 431, Ramona clay loam, taken near La Habra, California.
No. 7083, Dublin clay adobe, taken near Gilroy, California.
No. 3232, Glacial drift soil from Indiana.
No. 7680, Limestone soil, central Tennessee.
No. 11954, Cecil clay subsoil, Alabama.
All samples were saturated with Ca before grinding.

TABLE 6

Fusion analysis of soil colloids

	MILLIEQUIVALENTS PER 100 GM.			
	Ca	Mg	K	Na
431	58	68	20	11
7083	80	142	22	22
3232	60	38	25	15
7680	101	155	33	22
11954	14	20	7	7

The method depends upon the following principles: In crystalline substances, the constituent atoms are located at regularly spaced distances in the various directions, thus forming a regular three-dimensional space lattice. The regularly spaced atoms fall into planes and these planes are also regularly spaced. Because the interplanar spacings are of about the same order of magnitude

as the wave lengths of X-rays, the planes of atoms in a crystal are capable of acting as a diffraction grating for X-rays, in much the same way that the closely ruled lines on a glass plate diffract the waves of visible light. In the case of visible light, the wave length may be calculated from data which include knowledge of the spacings separating the lines which compose the grating. Similar application is made of the diffraction principle in X-ray crystal analysis, but in this case it is the wave length of monochromatic X-rays which must be known, while the quantity corresponding to the grating spacing is to be determined. This unknown quantity is the distance separating the planes of atoms in the crystal; it is the key to the whole problem of crystal structure.

When x-rays strike the atoms of a crystalline substance the rays are scattered in all directions, and in general these scattered rays are not intense enough to produce more than a slight fogging effect on a photographic film. If, on the other hand, a number of these scattered rays are deflected in such a manner that the deflected rays are in phase, their combined intensities will be sufficient to register on a stuitably placed film. It can be shown by simple trigonometry (1) that X-rays are deflected in phase from the atomic planes of a crystal when the relationship between the wave length of the X-rays (λ), the interplanar spacing (d) and the glancing angle Θ between the incident beam and the reflect ing plane is described by the equation:

$$n\lambda = 2d \sin \Theta$$

in which n is a simple integer representing the order of reflection. Accordingly, if the wave length, λ, be known and the glancing angle, Θ, be observable, it becomes possible to calculate d/n, that is, the ratio of the interplanar spacing to the order of reflection. Since n is a small integer and it is usually possible to decide whether it is 1, 2, or 3, etc., the value of the interplanar spacing is readily obtained.

In practice a single crystal, or a tube of the powdered crystals, is placed in the path of an X-ray beam, and the undeflected beam, as well as the various beams which are deflected in accordance with the foregoing equation, are intercepted and registered on a suitably placed photographic film or plate. From measurements on the film, the angular displacement of the beam ($= 2\Theta$) may be determined. If a single crystal is used with monochromatic X-rays, it is necessary to make a number of exposures with the crystal in different positions in order to obtain the various interplanar spacings, since for any one position we have fixed values for λ and Θ and consequently can have only one value for d/n. If, on the other hand, the sample is in the form of a fine powder, it consists of a large number of minute crystals in random arrangement, and some of the crystalline fragments, according to the law of probability, will have the required position with respect to the X-ray beam for any given interplanar spacing. Collectively, therefore, the particles will produce reflections in phase corresponding to all interplanar spacings present in the crystals.

It follows, then, that when powdered crystalline material is examined in an

X-ray diffraction apparatus, a series of lines is recorded on the photographic film, and that these lines correspond to the interplanar spacings of the material. This series of lines is known as the diffraction pattern and is characteristic of the substance which produces it. The production of a pattern is direct evidence that the substance is crystalline. Under favorable conditions the pattern may be interpreted so as to give a more or less complete picture of the structure of the crystalline substance.

The replaceable-base materials were examined in the form of fine powders that were passed through a wire sieve having 200 meshes to the linear inch. The samples were packed into thin walled glass tubes having a diameter of about 1 mm., and exposed in the X-ray diffraction apparatus supplied by the General Electric Company. A Coolidge tube with a molybdenum target was used as the source of X-rays and the X-rays were passed through a zirconium oxide screen so as to give monochromatic X-rays with a wave length of 0.712 Ångstrom units. The photographic film was placed on an arc of 8-inch radius, at the center of which was located the tube containing the specimen. The incident beam passed through a narrow slit (0.02 inch x 0.5 inch) and images of this slit were produced on the film by the undeflected beam and by the various deflected beams. By measuring the distance of the various lines from the "zero line," representing the intercept of the undeflected beam, values are obtained which are proportional to the angular displacement in radians.

Samples of bentonites from nine different sources, soil colloids from six different sources, and one sample each of beidellite and halloysite were examined by the powder method. All of these were examined in their original unground condition, some of them after prolonged grinding, some also after saturation with various replacing bases, and one after being heated to various temperatures.

QUALITATIVE REVIEW OF RESULTS

All of these substances showed distinct X-ray diffraction patterns, indicating that they are not amorphous, as has been commonly assumed, but, on the contrary, that they possess definitely crystalline structures. From a merely qualitative inspection it is apparent that there is a considerable similarity between all of the X-ray photographs, certain prominent lines being shown in all of the films (pl. 1 and 2). This suggests that all of these substances have some sort of a common structural basis. On the other hand, the films also show certain differences, both in the lines that are present and in the relative intensities of the lines. This suggests that within the common structural organization, there are certain atoms which, although fitting into the fundamental structure, are not essential to the framework and which give rise to additional reflecting planes that differ in the various samples.

The samples after prolonged grinding in a ball mill (usually 48 to 72 hours) gave X-ray patterns that were less distinct than those from the corresponding unground samples (pl. 3). In certain cases prolonged grinding apparently

produced no change in the pattern, although in some instances the lines almost completely disappeared, but usually the change was confined to only one or two lines in the pattern. The disappearance of a line caused by grinding was invariably accompanied by a darkening of that area of the film which corresponded to the position occupied by the missing line. This darkening effect indicates a broad scattering of the X-rays in the region involved, and signifies a partial breaking down of the crystalline material to an unorganized (i.e., an amorphous) condition. In every case the films of the ground material showed distinct increases in the fog effect, indicating that the grinding reduced more or less of the crystalline material to an amorphous condition.

A series of films was obtained representing bentonite 7 saturated with various replacing bases. All of the patterns were approximately alike (pl. 4, fig.1). A similar series of patterns for soil colloid 431 saturated with calcium, sodium, potassium, ammonium, magnesium, and copper showed no significant differences (pl. 4, fig. 2). That the substitution of one base for another failed to affect the X-ray films was probably because the base replacement, brought about by the treatment of the samples, was limited chiefly to the atoms located on or near the surface of the crystals. Apparently the interiors of the crystals were not affected by this treatment.

X-ray examination was made of four portions of bentonite 7 which had been heated to 350°, 450°, 600°, and 750°C., respectively (pl. 5). The diffraction patterns corresponding to the three lower temperatures were alike and similar to that of the unheated bentonite. The material heated at the highest temperature gave an altogether different and much fainter pattern containing a broad darkened area. This appears to indicate a considerable breaking down to amorphous material at the highest temperature with some alteration to a different type of crystal structure.

The bentonites from eight different sources gave diffraction patterns that are very similar (pl. 1, fig. 1), a number of prominent lines being common to all these films. We will discuss later certain minor differences in these patterns.

The soil colloids gave patterns obviously more complicated than the bentonite patterns, but nevertheless clearly related to them (pl. 1). The beidellite pattern is very similar to the bentonite patterns. The halloysite pattern suggests that of potash bentonite, although it contains fewer lines (pl. 2). These relationships will be discussed more fully in connection with the numerical data.

QUANTITATIVE INTERPRETATION OF RESULTS

As has already been indicated, the numerical values of the interplanar spacings may be obtained from measurements on the films. The films obtained from the various bentonites and soil colloids have been measured and the values of the interplanar spacings are given in tables 7 and 8. These values are expressed in Ångstrom units and opposite each value is an approximate indica-

TABLE 7

*Interplanar spacings of bentonite samples**

NO. 1	NO. 2	NO. 3	NO. 4	NO. 5	NO. 6	NO. 7	NO. 8	POTASH BENTONITE	BEIDELLITE	HALLOYSITE	CALCULATED SPACINGS FOR 9.0 Å UNIT CUBE	CORRESPONDING CRYSTALLOGRAPHIC INDEXES
5.20 w	5.10 w	.....	5.10 tr?	5.10 w	.....	5.20 w	5.10 w	5.00 w	.....	.....	5.19	(111)
4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.50 vs	4.45 vs	4.50	(100) [2]
.....	.....	.....	4.10 vs	.....	4.10 vvs	.....	4.00 w	.....	.....	.....	4.01	(120)
.....	.....	3.30 m	.....	.....	.....	.....	.....	3.65 m	.....	3.65 m	3.67	(112)
.....	.....	3.16 w	.....	3.20 m	.....	3.10 m	3.34 m	3.30 ?	3.30 ?	.....	3.18	(110) [2]
3.04 m	3.03 m	.....	3.08 m	.....	.....	.....	3.03 w	2.90 ?	.....	.....	3.00	(100) [3]
.....	.....	.....	.....	.....	2.86 vvw	.....	.....	.....	.....	.....	2.84	(130)
2.57 vs 2.51	2.58 vs 2.48	2.60 s 2.50	2.58 s 2.45	2.58 vs 2.52	2.58 s 2.45	2.62 s 2.52	2.58 vs 2.45	2.56 vs	2.60 s 2.52	2.60 m 2.35	2.60 2.49	(111) [2] (230)
.....	.....	.....	.....	.....	.....	2.28 w	.....	2.38 s	.....	.....	2.40	(123)
.....	2.24 tr	2.25 tr	2.24 ?	2.24 vvw	.....	2.24	.....	.....	2.24 vw	.....	2.25	(100) [4]
2.20 vvw	.....	.....	.....	.....	.....	.....	.....	2.22 vw	.....	.....	2.19	(140)
.....	.....	.....	.....	.....	.....	.....	.....	2.00 ?	.....	.....	2.00	(120) [2]
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.83	(112) [2]
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.73 1.67	(111) [3] (234)
1.69 w	1.70 m	1.69 m	1.69 m	1.69 m	1.70 m	1.71 m	1.69 m	1.70 vw	1.70 m	1.69 w		
.....	.....	.....	.....	.....	1.62 vw	.....	.....	1.63 w	.....	.....	1.64	(125)
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.54	(334)
1.50 vs	1.50 vs	1.50 vs	1.50 vs	1.50 vs	1.50 vs	1.51 vs	1.50 vs	1.50 vs	1.50 vs	1.48 s	1.50	(100) [6], (122) [2]
.....	.....	1.38 vvw	.....	.....	.....	.....	1.37 vw	.....	.....	.....	1.37	(335)
1.29 m	1.29 m	1.29 m	1.29 m	1.29 m	1.29 m	1.30 m	1.29 m	1.30 m	1.30 m	1.29 vw	1.30; 1.29	(111) [4]; (100) [7], (236)
1.24 w	1.25 w	1.24 w	1.25 w	1.24 w	1.24 w	1.25 w	1.24 w	1.24 w	1.24 w	1.24 vw	1.245	(230) [2]

* Interplanar spacings expressed in Ångstrom units. Symbols designate relative intensity of the corresponding lines. vvs = very very strong; vs = very strong; s = strong; m = medium; w = weak; vvw = very very weak; tr = trace; ? means line questionable. Bracketed values indicate a broad line which may be a composite of two or more superimposed lines. Figures in square brackets designate orders of reflection.

tion of the intensity of the line. The last two columns in each table are concerned with the interpretation of these data and will be referred to presently.

The general appearance of the patterns suggested that the structure might be a cubic lattice. In order to test this point quantitatively, a number of the spacing values were plotted and compared with charts, according to the method of Hull and Davey as outlined by Wychoff (8). Most of the values thus plotted agree with a cubic lattice based on a unit cube having an edge 9.0 Ångstrom units in length. Calculations were made of the interplanar spacings of the various reflecting planes in a theoretical cube of 9.0 Å. edge, and a list was prepared of all possible spacings between 9.0 Å. and 1.24 Å.

The last two columns of each table give the significant calculated values, together with their corresponding crystallographic indexes (Miller indexes). It will be seen that, with but few exceptions, the observed interplanar spacings agree closely with interplanar spacings calculated from the theoretical cube. Moreover, the observed relative intensities of the lines are similar to the expected intensities from the theoretical cube. From this agreement it is concluded that all of the substances examined have structures related to a cubic lattice with a unit cube having a 9 Å. edge. As some of the materials were obviously heterogeneous, the few lines which do not correspond to any spacings in the theoretical lattice may be ascribed to the presence of foreign material.

It will be observed that the bentonite patterns contain in general a smaller number of lines than the soil colloids, 9 to 14 lines being obtained in a bentonite pattern and 12 to 19 lines in a soil colloid pattern. Altogether 21 different lines are found in the bentonite patterns. All but one of these (the 3.30 to 3.34 Å. spacing) agree with spacings calculated on the theoretical cube. The soil colloid patterns contain a total of 30 different lines; five of these (7.40 Å., 5.80 Å., 4.30 Å., 3.80 Å., and 3.35 Å.) cannot be correlated with any calculated spacings of the theoretical cube, but the other spacings are in satisfactory agreement.

On the basis of the similarity of the crystallographic indexes, the various bentonite patterns may be grouped into classes having structures of varying complexity. The classes merge into one another somewhat and their separation is necessarily inexact and arbitrary. Nevertheless, the patterns fall distinctly into about three classes.

The simplest class includes the patterns of bentonites 1, 2, 7. The prominent lines of these patterns correspond to the following crystallographic indexes: (100), second, fourth, sixth, and seventh orders; (110), second order; (111), second and fourth orders; and second orders of (122) and (230). These observations suggest that the structure of these materials is related to a comparatively simple type of cubic lattice having atoms or groups of atoms at or near the corners of the cube. Chemical analysis shows that these samples have a composition closely approximating that given by Ross and Shannon for montmorillonite.

The next class in order of complexity includes bentonites 3, 4, 5, 6, and 8,

TABLE 8

*Interplanar spacings of soil colloids**

431	5696	7083	7680	3232	11954	CALCULATED SPACINGS FOR 9.0 Å UNIT CUBE	CORRESPONDING CRYSTALLOGRAPHIC INDEXES
.....	5.80 ?	.....	.....	.....	7.40 s	—	—
.....	.....	.....	.....	.....	.....	5.19	(111)
4.50 vs	4.50 vs	4.50 vs	4.50 m	4.50 s	4.60 vs	4.50	(100) [2]
.....	.....	.....	4.30 m	4.20 s	4.15	—	—
4.10 m	4.05 s	.....	.....	.....	.....	4.01	(120)
.....	.....	.....	.....	.....	.....	—	—
.....	3.75 m	.....	.....	.....	3.70 s	3.67	(112)
3.35 s	3.35 s	3.35 s	3.30 vvs	3.35 vvs	3.54	—	—
3.20 s	3.20 vvs	3.20 m	.....	.....	.....	3.18	(110) [2]
.....	3.00 w	3.00 w	3.00	.....	.....	3.00	(100) [3]
2.75 ?	.....	.....	2.80 vw	.....	2.70 m	2.71	(113)
2.64 s 2.56	2.64 vs 2.54	2.64 vs 2.54	2.58 w	2.56 m	2.58 vs 2.50	2.60	(111) [2]
2.44 s 2.40	2.45 m	2.45 s	2.46 vw	2.45 w	.....	2.49	(230)
.....	.....	.....	.....	.....	2.37 s	2.40	(123)
.....	2.28 vw	.....	2.25 vw	2.28 vw	2.31	2.25	(100) [4]
.....	.....	.....	.....	.....	2.22 m	2.19	(140)
2.18 w	.....	.....	.....	.....	.....	2.18	(223)
.....	2.13 vw	.....	2.13 w	2.12 m	.....	2.12	(110) [3]
2.00 w	2.03 vw	.....	1.99 vw	1.99 w	2.01 w	2.01	(120) [2]
.....	1.82 ?	.....	1.83 s	1.82 s	1.84 m	1.83	(112) [2]
.....	.....	.....	.....	.....	1.72 s	1.73	(111) [3]
1.70 m	1.66 ?	1.70 m	1.67 w	1.67 m	1.68	1.67	(234)
1.54 w	1.54 m	1.54 m	1.54 m	1.54 s	.....	1.54	(334)
1.51 s	1.50 s	1.51 s	1.50 s	1.50 s	1.50 vs	1.50	(100) [6], (122) [2]
.....	.....	.....	.....	.....	1.46 s	1.46	(116)
.....	1.38 w	1.38 w	1.38 vs	1.37 vs	.....	1.37	(335)
1.30 w	.....	1.30 w	.....	.....	.....	1.30	(111) [4]
.....	.....	.....	1.29 w	1.29 w	1.29 w	1.29	(236)
.....	.....	.....	1.25 vw	1.26 vw	1.24 w	1.245	(230) [2]

* For explanations see footnote table 7.

and the sample of beidellite. The diffraction patterns show the same lines as those of the first class and in addition two lines corresponding to crystallographic indexes (111), first order, and (100), third order, and a strong line corresponding to a spacing of 4.10 Å. Apparently these samples contain a greater concentration of atoms at fractional distances between the corners of the cubes than the first class. Bentonites 3 and 8 and the beidellite also show a spacing of 3.30 Å., but since this spacing does not correspond to any spacing in the theoretical cube, it was probably due to some impurity in the samples.

The potash bentonite sample apparently belongs in a separate class. Its pattern contains the same lines as bentonite 7, but, in addition it contains lines corresponding to the crystallographic indexes: (112), (123), (120) second order, and (125) and (140) first order. This suggests a considerably greater distribution of atoms at fractional distances between the corners of the unit cube than in the other classes of bentonites. The structure of halloysite appears to be similar to, although less complex than, potash bentonite.

Summarizing these conclusions, we may say that the patterns of the bentonites that have been examined appear to fall into three classes of varying complexity. The simplest class has a structure apparently related to a simple cubic lattice, (i.e., a lattice with the atoms or atomic groups mostly at or near the corners of the unit cube) since the prominent lines agree with simple crystallographic indexes. Other classes have lines agreeing with more complicated indexes, involving intercepts on 1/3, 1/4, 1/5, etc. of the unit edge, and the corresponding structures, although based on a unit cube of the same size, apparently have a considerably greater distribution of their constituent atoms at fractional distances between the corners of the cube.

As has been intimated, the X-ray evidence indicates that the soil colloids possess a more complex structure and are more heterogeneous than the bentonites. Each of the soil colloid patterns contains all of the lines of at least one bentonite pattern, and some contain all of the lines of two different bentonite patterns; in addition, each contains lines foreign to the bentonite patterns but related to the unit cube; and, finally, each contains several lines not related to the unit cube. This suggests that the soil colloids may be composed of one or more bentonite or similar substances mixed with non-bentonitic material.

Because of the obvious heterogeneity of the soil colloids and the faintness and uncertainty of some of the lines, it has been found impracticable to classify the soil colloid pattern. As distinguished from bentonites, the soil colloids (with one exception) are characterized by the presence of a 1.54 Å. spacing corresponding to crystallographic index (334). Soil colloids 431 and 7083 showed the simplest diffraction patterns and are very similar to that of the potash bentonite. The pattern of soil colloid 5696 is somewhat more complex, but still it resembles that of potash bentonite (compare pl. 1, fig. 2, and pl. 2). Two of these colloids, 431 and 7083, were separated from California soils, and the third, 5696, came from Nevada; they, therefore, represent semiarid soils. The

other samples representing soils from the humid sections of America are obviously more complex structurally.

After the preceding part of this paper had been written Hendricks and Fry kindly sent us a copy of their unpublished manuscript entitled, "The results of X-ray and microscopic examination of soil colloids." This paper has subsequently been published (4). Their X-ray photographs are not strictly comparable with ours for the reason that they used a copper target, whereas we employed a molybdenum target, and also the size and types of cassettes used by them were different from ours. The calculated spacings reported in table 4, 5, 6, and 7 of their paper are in substantial agreement with those recorded in our tables 7 and 8. The montmorillonite pattern of Hendricks and Fry agrees with those of bentonite 1, 2, and 7, and the so-called Ordivician bentonite showed an exotic 3.30 spacing just as do our bentonites 3 and 8 and the potash bentonite. They suggest that the Ordivician bentonite was contaminated with quartz. As some of our materials may also have contained small quantities of quartz, it is possible to account for some of the stray lines on that basis.

In order to obtain further evidence on this point, an X-ray powder diagram was made of a sample of ground quartz. The pattern showed lines corresponding to a very, very strong 3.35 Å. spacing and to strong 4.30, 1.80, and 1.37 Å. spacings, as well as a number of weaker lines. The four strong lines might be expected to contribute to a pattern if present as an impurity, even if only in comparatively small proportion. It is interesting to note that bentonites 3 and 8, beidellite, and all of the soil colloids show evidence of quartz contamination by the presence of one or more of these lines.

We have confirmed the conclusions of Hendricks and Fry that beidellite is structurally very similar to bentonite. Their kaolinite pattern, however, is distinctly different from our bentonite patterns.

THE ZEOLITES

The term "zeolite" is often employed in discussions on the base-exchange property of soils and much use has been made by soil investigators of the synthetic preparation known as permutite or synthetic zeolite. As is well-known, permutite possesses marked base-exchange power and is undoubtedly similar in certain respects to the base-exchange material of soils. Burgess (2) holds that the calcium form of the permutite which he has synthetized is identical chemically with the natural zeolite known as scolecite.

We have investigated several natural zeolites, with the results shown in table 9. The samples used in these experiments were ground to a moderate extent only and were still definitely crystalline, as was indicated by X-ray examination. Nevertheless, practically all of the bases of stilbite were replaceable and also a very large part of those of the other zeolites. In this respect the natural zeolites differ markedly from the bentonites and the soil colloids that we have investigated. As has been pointed out already, relatively little

magnesium of the soil colloids is replaceable and much of the magnesium of bentonite cannot be replaced unless the material is ground to extreme fineness. Practically all of the bases contained in crystalline heulandite and analcite are also replaceable.

Another important difference between the natural zeolites, and bentonite and soil colloids, is found in their content of magnesium. As already shown, the bentonites are primarily magnesium compounds and the soil colloids discussed in this paper are closely related to the bentonites. This is not true, however, of the zeolites. As far as we are aware no natural magnesium zeolite has ever been reported.

X-ray studies on natural zeolites

The following is a list of the zeolites that have been examined by the X-ray method, together with the crystallographic systems in which mineralogists classify them:

Analcite	Cubic
Natrolite	Orthorhombic
Heulandite	Monoclinic
Stilbite	Monoclinic
Scolecite	Monoclinic

All of these substances gave good X-ray patterns. As might be expected from the diverse crystallographic systems to which they belong, there is a corresponding diversity in the appearances of the patterns. It is significant that none of these patterns resembles the typical patterns of the bentonites and soil colloids; consequently their base-exchange properties cannot be due to the same substances.

It might be expected that, since analcite and the bentonites belong to the same crystallographic system (cubic), the base replacement mechanism would be essentially the same in both. However, chemical studies have shown that there is a distinct difference in the behavior of these substances, complete replacement in the bentonites taking place only after prolonged grinding, whereas the bases of analcite are readily replaced with only moderate grinding treatment. The analcite structure appears to be based on a larger unit cube than the bentonites and it is possible that the difference in lattice dimensions may account for the easier replacement in analcite, since a more open structure in this substance would presumably permit a readier movement of bases within the lattice.

Several samples of synthetic permutite have also been examined with the X-ray, but, in agreement with the results of other investigators, none of these materials gave a diffraction pattern. Evidently these substances are amorphous.

Effect of heat

Numerous studies made here and elsewhere indicate that the inorganic base-exchange material of soils is a comparatively stable substance. For example the bases may be completely replaced by H ions, upon treatment with a dilute acid, without effecting decomposition of the base-exchange material to any great extent. In view of the data presented already, the fact that both the bentonites and the soil colloids are known to absorb water very readily, and that the base-exchange material of bentonite probably contains water of crystallization, a few experiments were made with reference to the effect of heat on these materials.

TABLE 9

Total bases and replaceable bases of natural zeolites

	MILLIEQUIVALENTS PER 100 GM.							
	Total bases				Replaceable bases			
	Ca	Mg	K	Na	Ca	Mg	K	Na
Natrolite	90	9	8	352	42	6	7.5	254
Stilbite	263	6	5	63	265	4	4.5	44
Scolecite	360	10	13	33	208	Trace	8.0	16

TABLE 10

Effect of heat on bentonites, soil colloids, and natural zeolites

TEMPERATURE	MILLIEQUIVALENTS OF TOTAL REPLACEABLE BASES (NH_4 ABSORBED)					
	Bentonite No. 7	Bentonite No. 3	Soil Colloid 7083	Natrolite	Stilbite	Scolecite
°C.						
Not heated	105.0	86.0	56	221.5	312.0	213.0
350	103.0	88.0	54	102.0	19.7	12.2
500	95.0	76.0	..	98.0	.....	12.5
600	52.5	19.2	19	.....	.....	.....
750	2.2	2.5	..	.....	.....	.....

The data reported in table 10 show that the soil colloids and bentonites are remarkably stable toward heat. The heating experiments were conducted in a muffle furnace controlled by a pyrometer, the samples being held in the furnace at each temperature until constancy of weight was attained. It will be noted that the temperature of 350°C. produced no effect on the replaceable bases of the soil colloid and bentonites. Above this temperature there was a gradual falling off in the content of replaceable bases, until at a temperature of 750°C. the base-exchange power was practically destroyed. On the other hand, the zeolites behaved very differently. Their power to undergo an exchange of bases with a salt solution was greatly reduced by heating to a temperature of 350°C.

It is difficult to harmonize the results of this investigation with those obtained by Steemkamp (6), who reported that the content of replaceable bases of certain soils of England is materially affected by dehydration. It is possible that the changes noted by Steemkamp were occasioned by the organic part of the exchange substance. However, we have thus far been unable to verify Steemkamp's conclusions.

A striking difference is also brought out by heating these materials to a temperature of 100°C. Both the bentonites and soil colloids lose about 10 per cent of their air-dried weight at 100°C., whereas the natural zeolites lose much less water at this temperature.

The natural zeolites are considered by mineralogists to be hydrous aluminosilicates, formed as a result of the weathering of feldspars. From a geological point of view the zeolites are relatively unstable substances. On the other hand, the clay minerals are relatively stable chemically. The colloidal material of soils is undoubtedly the most highly weathered part of the soil, representing as it does the material that is left behind after the less stable and more soluble substances have been removed by percolating water. When we consider the circumstances under which soils are formed and the conditions to which they are subjected in the natural state, it is evident that those constituents which persist in the soil must be relatively stable substances. In the event that one or more of the natural zeolites should be laid down with the soil forming materials, or be formed in the soil mass as a result of weathering processes, they would probably undergo complete decomposition under the conditions which bring about the development of a relatively mature soil profile.

GENERAL DISCUSSION

The foregoing data seem to justify the definite conclusion that the substances composing the colloidal material of the soils that have been investigated are not amorphous, as has been commonly assumed, but on the contrary that they are composed chiefly of crystalline substances. It is interesting that Hendricks and Fry (4) have found by microscopic and X-ray examination that the colloidal materials separated from many different types of soils from various parts of the United States contain definitely crystalline bodies. In agreement with our conclusions, they hold that the crystalline materials of the soil colloids examined by them belong to the clay minerals. Their results indicate that certain of the soil colloids are closely related to the montmorillonite-beidellite clays, others are similar to the potash bentonites, referred to by them as Ordivician bentonite; whereas still others are related to the halloysite type of clay minerals. Every sample which they examined was found to contain definitely crystalline material.

We have found that the replaceable bases occur not only on the surface of colloidal particles but also on the interior of the crystals. Since the X-ray analyses indicate an orderly arrangement of the atoms within the particles, and

since the exchange of bases is stoichiometric, it is safe to conclude that the base-exchange substances are true chemical compounds. The replaceable bases, therefore, are not merely adsorbed on the surface of the particles, rather the bases are an integral part of the chemical constitution of the crystals.

Ross and Shannon (5) and Wherry (7) have concluded that the crystals of colloidal bentonite are lamellar in form. Since it is only the bases that occur on or near the surface of the crystals that can be replaced, the ratio which we have found between the replaceable bases and the total base content of the unground samples of bentonite is consistent with this conclusion. The X-ray evidence as to the cubical form of the crystal lattice is also consistent with this view. It is possible that the crystalline soil colloidal material is also lamellar.

It should be pointed out, in this connection, that the double-refractive power of bentonite and various soil colloids, which has been reported by Ross and Shannon (5), Hendricks and Fry (4), and several European investigators, indicates that the crystal structure of these materials is not strictly cubical. At present, it is not possible to explain the seeming conflict of evidence on this point. It is possible that the crystal lattice is pseudo-cubic, rather than exactly cubic in form. On the other hand, certain crystalline materials, when present in the form of fine needles or thin plates, have been found to be double-refractive and at the same time to possess cubical lattice structures.

The chemical and X-ray data clearly establish the fact that the inorganic soil colloids are not zeolites. It is interesting in this connection that Gedroiz (3) has recently pointed out that the inorganic base-exchange material of soils is not zeolitic (*ungenau auch zeolithischer Teil des Bodens genannt*), on the contrary, these colloids apparently belong to the group of minerals known to mineralogists as clays. Certain of the better known clay minerals, such as kaolinite, and the less well known anauxite, are hydrogen aluminum silicates, which do not possess important base-exchange powers. On the other hand, the mortmorillonite-beidellite group of clay minerals, which characterizes the bentonites, are essentially crystalline magnesium aluminum silicates. Apparently the magnesium may be partially substituted by potassium either before crystallization takes place or subsequently, with the resulting formation of a magnesium potassium aluminum silicate. The bases that occur on or near the surface of the crystals may be replaced by calcium or sodium in the natural state, but the results of grinding experiments demonstrate that calcium and sodium do not extend into the centers of the crystals.

The Cecil colloid represents one of the oldest soil formations on the American continent. It has been derived from igneous parent material, either granite or rocks that are closely related to the granites. This colloid is characterized by a relatively low base-exchange capacity and low total base content. As pointed out in the foregoing, the crystalline material of this colloid is distinctly acidic. Hendricks and Fry (4) have investigated several samples of Cecil colloids and have concluded that they are closely related to the halloysite type of clays. Our results on a single sample of Cecil colloid are consis-

tent with this view. It is interesting to note that halloysite contains notable amounts of replaceable H ions, and the same is true of the Cecil colloid.

As is well known, the chief replaceable base of normal soils is usually calcium, This is probably because of two facts: (1) Calcium ions possess a relatively high energy of replacement, and (2) The soil solutions which come into contact with the colloidal particles contain more or less dissolved calcium derived from the weathering of various calcium minerals, including calcium carbonate. One or more of the calcium minerals are almost universally laid down with the soil-forming materials. The result is that calcium brought into solution subsequently by weathering agents, replaces more or less of the magnesium from the surface of the clay minerals. In the case of alkali soils, which contain relatively high concentrations of sodium salts, the bases that occur on or near the surfaces of the crystals are replaced in considerable part by sodium.

Soil colloid 431 represents a soil of granitic origin that was formed within a relatively recent geological period under conditions of limited rainfall. As pointed out already, the Cecil soil was also derived from granitic rock, but has been subjected to prolonged weathering under a humid climate. It is interesting that soil colloid 431 is related to the bentonites, whereas according to Hendricks and Fry the Cecil soil resembles halloysite.

It seems appropriate to state that this investigation has not been sufficiently extensive to warrant conclusions as to the nature of the base-exchange material in soils everywhere. The essential agreement between our results and those of Hendricks and Fry, based on a study of a much wider range of soil colloids, suggests, however, that the few samples which we have investigated are widely representative. We expect to expand this work so as to include a wider range of soils.

As stated already, Burgess (2) claims that the permutite which he has synthesized is identical chemically with the natural zeolite known as scolectite. If this be true, it is safe to say that the synthetic material differs materially from the base-exchange substance of soils that we have examined. As a matter of fact there is some question whether the synthetic preparation is actually identical chemically with scolecite. It seems that Burgess' conclusion was based primarily on the fact that the synthetic substance has the same percentage composition as scolecite. Such evidence, however, is not sufficient to establish chemical identity, for it is well-known, for example, that the percentage composition of the various hexose sugars is the same, yet some of these sugars are ketones whereas others are aldehydes. Among the silicates the ratio of Al_2O_3:SiO_2 in many different minerals is practically identical.

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(4) HENDRICKS, S. B., AND FRY, W. H. 1930 The results of X-ray and microscopic examinations of soil colloids. *Soil Sci.* 29: 457–479.

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(6) STEEMKAMP, J. L. 1928 The effect of dehydration of soils upon their colloid constituents. *Soil Sci.* 25: 163–182.

(7) WHERRY, E. T. 1925 Bentonite as a one-dimensional colloid. *Amer. Mineralogist* 10: 120–123.

(8) WYCKOFF, R. W. G. 1924 The Structure of Crystals, p. 190–195. Chemical Catalog Co., New York.

PLATE 1

X-RAY DIFFRACTION PATTERNS OF BENTONITES AND SOIL COLLOIDS

FIG. 1. Interplanar spacings of different samples of bentonite.
FIG. 2. The structural similarity between bentonites and soil colloids.

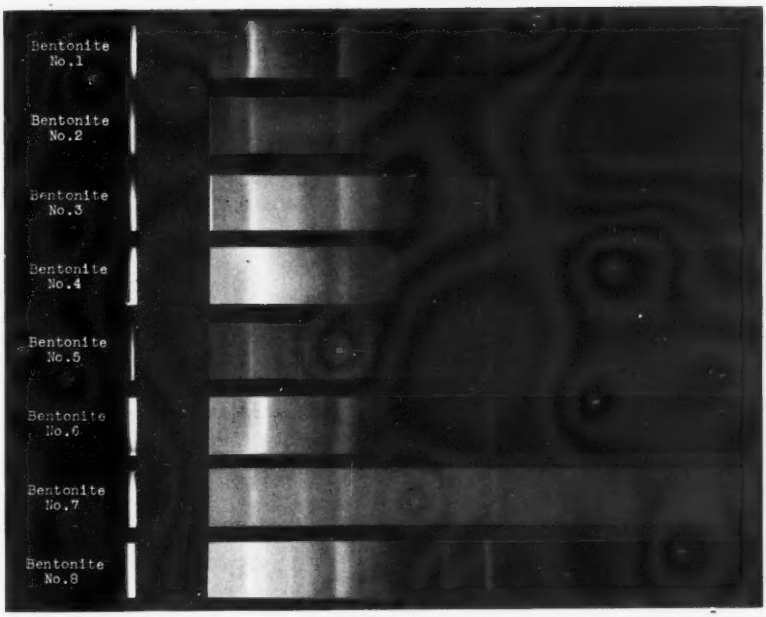

Bentonite No.1
Bentonite No.2
Bentonite No.3
Bentonite No.4
Bentonite No.5
Bentonite No.6
Bentonite No.7
Bentonite No.8

FIG. 1

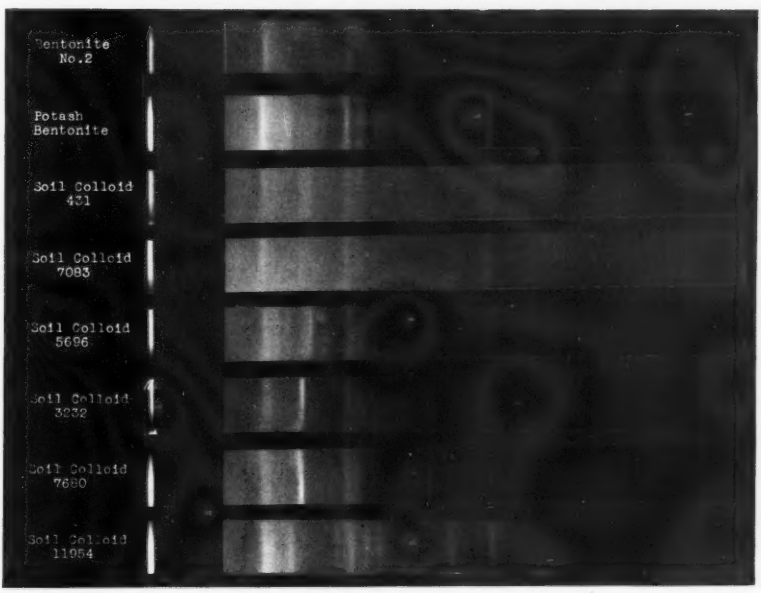

Bentonite No.2
Potash Bentonite
Soil Colloid 431
Soil Colloid 7083
Soil Colloid 5696
Soil Colloid 3232
Soil Colloid 7680
Soil Colloid 11054

FIG. 2

PLATE 2

THE STRUCTURAL RELATIONSHIP OF DIFFERENT CLAY MINERALS

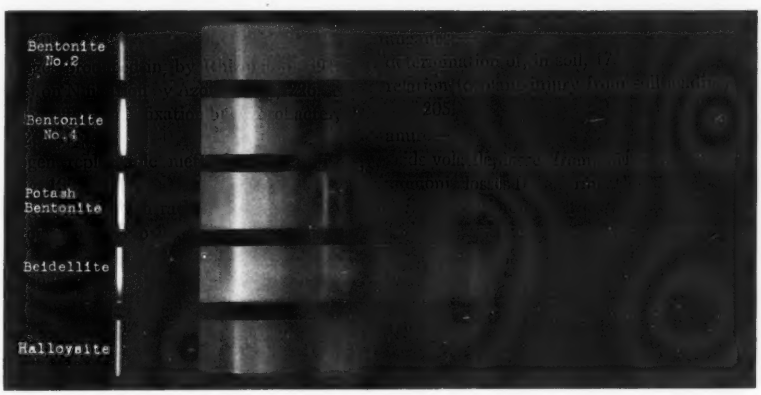

Bentonite No.2
Bentonite No.4
Potash Bentonite
Beidellite
Halloysite

PLATE 3

X-RAY DIFFRACTION PATTERNS OF BENTONITE AND SOIL COLLOIDS AS AFFECTED BY GRINDING

FIG. 1. The crystalline structure of bentonites as affected by grinding.
FIG. 2. The crystalline structure of soil colloids as affected by grinding.

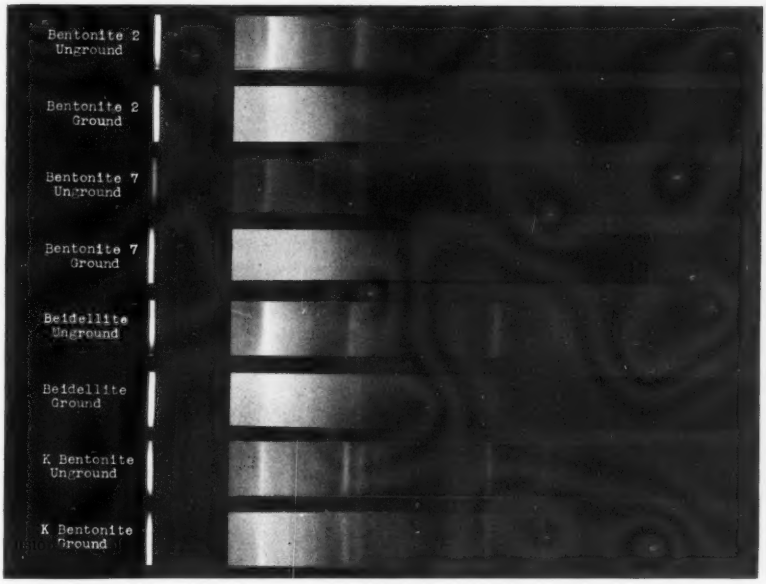

Bentonite 2 Unground
Bentonite 2 Ground
Bentonite 7 Unground
Bentonite 7 Ground
Beidellite Unground
Beidellite Ground
K Bentonite Unground
K Bentonite Ground

FIG. 1

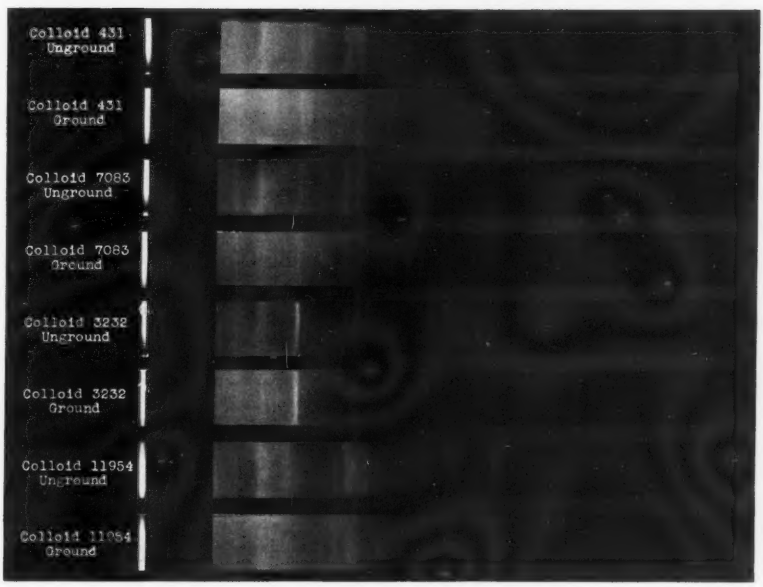

Colloid 431 Unground
Colloid 431 Ground
Colloid 7083 Unground
Colloid 7083 Ground
Colloid 3232 Unground
Colloid 3232 Ground
Colloid 11954 Unground
Colloid 11954 Ground

FIG. 2

PLATE 4

X-RAY DIFFRACTION PATTERNS OF BENTONITE AND SOIL COLLOIDS AS AFFECTED BY BASE-REPLACEMENT

FIG. 1. Crystalline structure of bentonite as affected by base replacement.
FIG. 2. Crystalline structure of soil colloids as affected by base replacement.

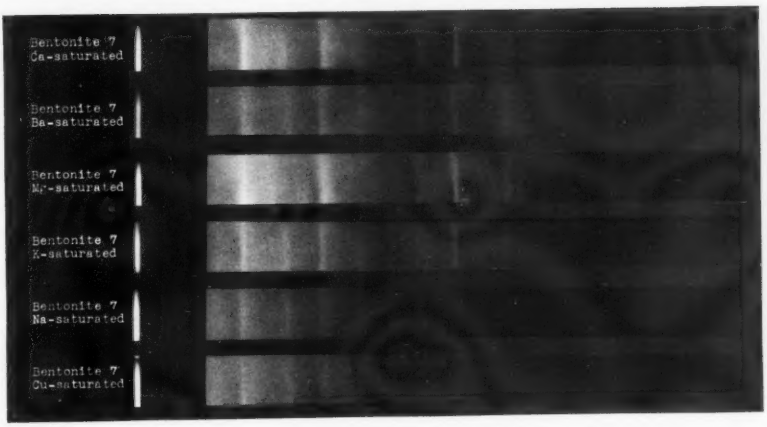

Bentonite 7
Ca-saturated
Bentonite 7
Ba-saturated
Bentonite 7
Mg-saturated
Bentonite 7
K-saturated
Bentonite 7
Na-saturated
Bentonite 7
Cu-saturated

FIG. 1

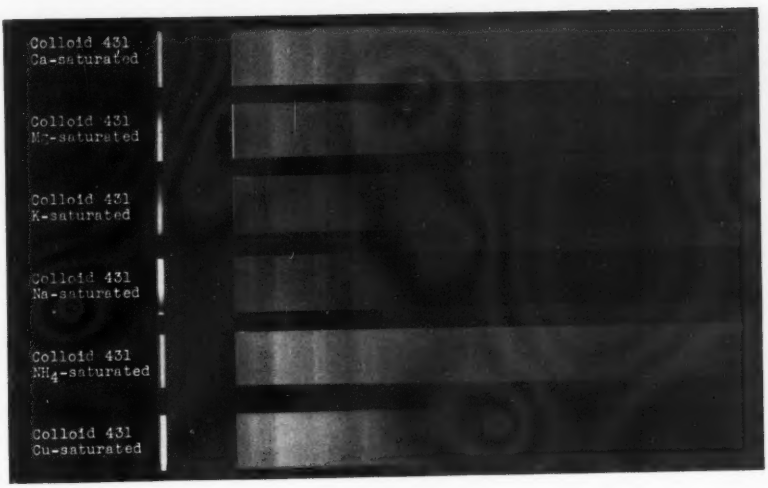
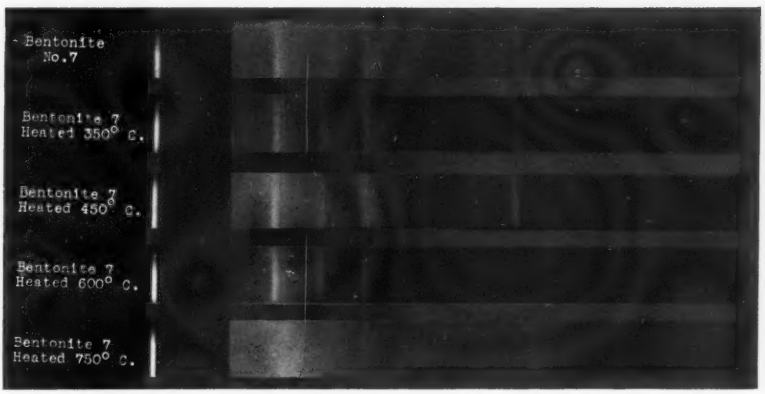

Colloid 431
Ca-saturated
Colloid 431
Mg-saturated
Colloid 431
K-saturated
Colloid 431
Na-saturated
Colloid 431
NH_4-saturated
Colloid 431
Cu-saturated

FIG. 2

PLATE 5

EFFECT OF HEAT ON THE CRYSTALLINE STRUCTURE OF BENTONITE


Bentonite No.7
Bentonite 7 Heated 350° C.
Bentonite 7 Heated 450° C.
Bentonite 7 Heated 600° C.
Bentonite 7 Heated 750° C.

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: IV. ISOELECTRIC PRECIPITATES[1]

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In the preceding section (Part III) of this series the isoelectric precipitates of aluminum and ferric "hydroxides," "phosphates," and "silicates" were discussed. In the present paper we shall deal with another class of isoelectric precipitates which are no less important for an understanding of soil processes, the so-called "humates."

The soil organic matter known as humus possesses acidic or acidoid properties, combining with bases to form "humates." These substances have been subjected to an extensive physico-chemical investigation by Odén (6), who regards them as true acids in contradistinction to the adsorption theory of Baumann and Gully (1). Whether the acid nature of humic substances is due to replaceable carboxyl hydrogen, or to hydroxyl hydrogen as in the phenols, or to hydro-carbon hydrogen as in aceto-acetic and malonic ester, or to the hydrogen of the water activated through a fixation of the hydroxyl group, is of no significance for our present study.

Humus combines with, and neutralizes bases, and resembles in this and other respects silicic, oleic, and other weak acids. It is also distinctly electronegative, migrating toward the anode in a solution of any pH. It is readily dispersible when free from electrolytes. The alkali "humates" are extremely dispersible, bordering on true solution if not actually attaining it. The "humates" of the divalent cations are not so highly dispersible. All are electronegative. The aluminum and ferric "humates," which are our present object of study, are amphoteric, and are non-dispersible at or near the iso-electric point but become highly dispersible with increasing positive or negative charge.

The neutralizing equivalent (and cation exchange capacity at the point of neutrality) of the humus acids is very high—about three times higher than that of the highly silicated mineral soil colloids such as bentonite, the equivalent of which is about 1,000 gm. (per gram equivalent base). Odén found the equivalent for "humic acid" to be about 330. For "hymatomelanic acid" (the alcohol-soluble component) he found a value of 220 by the use of various methods 7). For a sample of "humic acid" prepared according to the method of Odén, the author found an exchange capacity of 3.064 milliequivalents per gram,

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

which yields an equivalent of 326. There seems therefore to be a remarkable constancy in the neutralizing power of this complex. Where the more inactive "humin" (humuskohle) colloids were not separated from the alkali "humate" (by flocculation with NaCl) Odén found a higher equivalent. "Humic acid" from young peats shows a lower equivalent because of the presence of pectinic acids. A lower equivalent is also found whenever the "hymatomelanic acid" is not separated. For Merck's "acidum huminicum" Odén found equivalent weights between 200 and 300. "Raw humic acid" yielded values between 250 and 400 according to its origin.

Regarding the constitution of the humus complex we know nothing. Which of, and to what extent, the various organic constituents known to be present in the colloid are responsible for its acid nature is of the greatest importance for our present study. Since the relative proportions of these components vary with the nature of the original plant material, with the stage of transformation, and with the climatic and microbiologic conditions, under which the material is formed, it is obvious that there can be no constant equivalent for the humus colloid as a whole.

In the following experiments the total alkali dispersible colloid was employed. In experiments now in progress an attempt is being made to study the various components of humus from the colloid chemical standpoint. The various components of humus reported as "hemicellulose," "cellulose," and "lignin" may be very different from the corresponding materials present in the original plants in which they were synthesized. Oxidation and reduction, substitution and addition derivatives, and lactone formation would result in combinations possessing very different properties. It must be remembered that in the methods of analysis now in vogue, these delicately complex and reactive materials are subjected to such a drastic treatment that any conclusion as to their original make-up is extremely hazardous.

PREPARATION OF "Na-HUMATE"

The peat from which the humus colloid was obtained was supplied by Dr. C. E. Skinner whose description of the material reads:

> Black spruce bog, Lewis Township, Mille Lacs County, Minnesota; pH 4.0 or below, ash low (about 5 per cent), stratum of black spruce and tamarack; shrub stratum of Ledum, lowest stratum of living sphagnum. This is a true sphagnum bog, but is underlaid with remains of sedge peat. It is an uncultivated virgin bog.

Two kilos of the moist peat were digested with 1,250 cc. strong ammonia in 18 liters of distilled water, shaken, and let stand for two months. The liquid was then siphoned off from the sediment and acidified with a large excess of HCl. The precipitate was then washed on the filter until the colloid started to disperse freely. It was then placed in a large electrodialysis cell, the central compartment of which measured 10 by 13 inches and $\frac{3}{4}$ inch in thickness. The cell was put in a 110 volt D.C. circuit in series with three 100-watt lamps

placed in parallel. The current was about 2 amperes at the beginning and fell to a fraction of an ampere at the end of three days when the diffusible ions were practically all removed.

A sample of the electrodioalyzed humus, which yielded 1.12 per cent ash, was then treated on the filter with a normal solution of neutral Ca-acetate until the filtrate gave a neutral reaction, and then once with $CaCl_2$. It was then washed until the Cl-ion reaction disappeared. The Ca was now displaced with normal NH_4Cl and the Ca determined in the filtrate. The base exchange capacity was 2.857 milliequivalents per gram, which gives an equivalent weight of 350.

A "Na-humate" solution was now prepared by adding 100 cc. *N* NaOH to a suspension containing 35 gm. dry weight of the electrodialyzed humus and diluting to 1 liter. This makes a 0.1 *N* solution of Na-humate *with respect to the Na ion.*

THE ISOELECTRIC "HUMATES" OF ALUMINUM AND IRON

A series of these precipitates were prepared by mixing varying proportions of "Na-humate" with aluminum and ferric chlorides as described in the preceding section (part III: Isoelectric precipitates) in this journal. The pH was adjusted to the isoelectric point by adding NaOH to the Na-humate or HCl to the chlorides, as the case required, before the mixing of these solutions. The results are shown in tables 48 to 53b.

Starting with a mixture of three milliequivalents of $AlCl_3$ to three of Na-humate, as in table 48, we see that the system remains electronegative over the entire range of pH values, which covers the zone of most rapid flocculation. If we assumed that each equivalent of "humate" displaces quantitatively one equivalent of Cl, we would expect the complex with the aforementioned proportions to remain electronegative because the humate ion would probably not be dissociated by the complex. The humate systems differ from the silicate and phosphate systems in that the humus, which is colloidal, is completely precipitated with the aluminum and ferric "humate" complex, leaving, in all cases, a colorless solution. But it is very doubtful whether all the humus combines with the metal ions. We are probably dealing with an equilibrium reaction similar to the reactions with the phosphate and silicate. Since the free humus is carried down with the precipitate there is no direct way of telling to what extent combination takes place, but, as we shall see later, this information comes in an indirect and very interesting way (section V).

The OH ions undoubtedy compete with the humate as with the phosphate and silicate ions and the diffusible Cl ions probably persist in the complex up to fairly high pH values. The fact that the complex in table 48 remains negative must be due to the condition that the anionic dissociation of the Cl ions is more than balanced by the cationic dissociation of the free humus complex.

Passing now to a proportion of six milliequivalents of Al to three of the humate, as in table 49, we note that the complex becomes isoelectric between a pH

5.0 and 4.2, is weakly positive at 4.2 and returns to the isoelectric conditions again at a pH of 3.8. At still lower pH values it remains weakly negative. We

TABLE 48

The $AlCl_3$ + Na-humate, system no. 51

A. 1.0 millimol $AlCl_3$ in 1,000 cc.

B. 3.0 millimols Na-humate in 1,000 cc.

SOLUTION A, 20 cc. + HCl MILLIMOLS*	SOLUTION B	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
	cc.				
0.0	20	Slow	xx	.....	...
0.005	20	Instant	xxxx	−1.26	4.5
0.01	20	Instant	xxxx	−1.00	4.2
0.03	20	Instant	xxxx	−0.53	3.7
0.05	20	Instant	xxxx	.....	...
0.10	20	Rapid	xxxx	−0.49	...
0.15	20	Rapid	xxxx	.....	...
0.30	20	Rapid	xxxx	−0.23	...

* Plus enough water to make a total volume of 50 cc.

TABLE 49

The $AlCl_3$ + Na-humate, system no. 52

A. 2.0 millimols $AlCl_3$ in 1,000 cc.

B. 3.0 millimols Na-humate in 1,000 cc.

SOLUTION A, 20 cc. + HCl MILLIMOLS	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
0.0	0.075	0	0	.....	...
0.0	0.065	0	x	.....	...
0.0	0.060	Rapid	xxx	−1.95	...
0.0	0.050	Instant	xxxx	−0.38	5.0
0.0	0.025	Instant	xxxx	+0.18	4.2
0.0	0.0	Instant	xxxx	±0.0	3.8
0.05	0.0	Rapid	xxxx	−0.15	...
0.15	0.0	Rapid	xxxx	.....	...
0.30	0.0	Rapid	xxxx	−0.23	...

Isoelectric mixture:

2.0 millimols $AlCl_3$ in 1,000 cc.

3.0 millimols Na-humate + 1.65 millimols NaOH in 1,500 cc.

pH 4.5.

Al_2O_3 in solution: 0.195 millimol.

Humus in solution: None.

Composition of floc: $\frac{1.05 \text{ gm. humus}}{0.805 \text{ millimol } Al_2O_3} = 1.305$ gm. humus per millimols Al_2O_3.

have here hit upon a proportion in which the amphoteric character of the complex is just developing. There are here two isoelectric points. There is

just a slight dip across the isoelectric line and then a return to the negative condition, as it is shown in figure 8.

This return to the negative condition was not observed in the aluminum and ferric "phosphates" and "silicates." The reason for this difference in behavior is to be sought in the colloidal nature of the humus complex itself. When the pH in the phosphate and silicate system is lowered these complexes become increasingly electropositive because the diffusible Cl ions, highly dissociated by the complex, enter in ever-increasing numbers until the complex undergoes a complete molecular and ionic dispersion. Neither the anions nor the cations remain colloid-dispersed [except in concentrated silicate systems where

TABLE 50

The $AlCl_3$ + Na-humate, system no. 53

A. 4.0 millimols $AlCl_3$ in 1,000 cc.

B. 3.0 millimols Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.19	0	x	.....	...
20	0.18	Rapid	xxxx	−1.38	5.8
20	0.16	Instant	xxxx	+0.84	4.75
20	0.14	Instant	xxxx	+1.18	4.5
20	0.12	Instant	xxxx	+1.18	4.4
20	0.10	Instant	xxxx	+1.02	4.3
20	0.05	Instant	xxxx	+0.80	4.2
20	0.0	Instant	xxxx	+0.34	3.8

Isoelectric mixture:

4.0 millimols $AlCl_3$ in 1,000 cc.

3.0 millimols Na-humate + 8.38 millimols NaOH in 1,500 cc.

pH 5.15.

Al_2O_3 in solution: 0.029 millimol

Humus in solution: None.

Composition of floc: $\frac{1.05 \text{ gm. humus}}{1.971 \text{ millimols } Al_2O_3} = 0.533$ gm. humus per millimols Al_2O_3.

a decrease in the positive or an increase in the negative charge of the remaining complex may be observed at low pH values (5)].

In the humate systems, in which the negative component is almost wholly colloidal, the effect of a lowering of the pH will be in two directions. The amphoteric sesquioxide component will become more strongly electropositive as the number of Cl ions in combination increases and the positive charge of the complex will therefore increase at first. But as the solubility of this component increases with the chloridation it becomes quantitatively weaker and the complex as a whole will grow less positive or more negative because the negative component (humus) remains colloid-dispersed in the complex.

TABLE 51A

The $AlCl_3$ + Na-humate, system no. 54

A. 8.0 millimols $AlCl_3$ in 1,000 cc.

B. 3.0 millimols Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.44	0	x	.....	...
20	0.42	Rapid	xxx	−1.90	...
20	0.40	Instant	xxxx	−0.98	6.1
20	0.38	Instant	xxxx	+1.44	4.8
20	0.36	Instant	xxxx	+2.16	4.5
20	0.34	Instant	xxx	+2.16	4.4
20	0.32	Instant	xxx	+2.02	4.35
20	0.20	Instant	xxxx	+1.90	4.3
20	0.0	Instant	xxxx	+0.67	3.8

Isoelectric mixture:

8.0 millimols $AlCl_3$ in 1,000 cc.

3.0 millimols Na humate + 19.6 millimols NaOH in 1,500 cc.

pH 5.5.

Al_2O_3 in solution: 0.039 millimols.

Humus in solution: None.

Composition of floc: $\frac{1.05 \text{ gm. humus}}{3.961 \text{ millimol } Al_2O_3} = 0.265$ gm. humus per millimol Al_2O_3.

TABLE 51B

The $FeCl_3$ + Na-humate, system no. 55

A. 8.0 millimols $FeCl_3$ in 1,000 cc.

B. 3.0 millimols Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.44	0	x	.....	...
20	0.42	Rapid	xxx	−2.33	6.0
20	0.40	Instant	xxxx	−1.00	5.1
20	0.38	Instant	xxxx	+0.87	4.0
20	0.36	Instant	xxxx	.....	3.5
20	0.34	Instant	xxxx	+2.02	3.3
20	0.30	Rapid	xxxx	.....	...
20	0.20	Slow	xxxx	+1.89	...
20	0.10	Slow	xxxx	.....	...
20	0.0	Rapid	xxx	+1.60	...

Isoelectric mixture:

8.0 millimols $FeCl_3$ in 1,000 cc.

3.0 millimols Na-humate + 19.46 millimols NaOH in 1,500 cc.

pH 4.55.

Fe_2O_3 in solution: 0.212 millimol.

Humus in solution: None.

Composition of floc: $\frac{1.05 \text{ gm. humus}}{3.788 \text{ millimols } Fe_2O_3} = 0.277$ gm. humus per millimol Fe_2O_3.

The two isoelectric points in table 49 differ electrokinetically as follows: At the first point, pH 4.5, the electropositive component is quantitatively greater but qualitatively weaker than at the second point, pH 3.8. The total number of positive charges is not necessarily the same, because the cationic dissociation of the humus complex undoubtedly varies with the pH. It is generally maintained that the tri-valent cations are responsible for the positive charge. If this were so then the positive charge should increase as these cations become more numerous with a lowering of the pH.

TABLE 52A

The $AlCl_3$ + Na-humate, system no. 56

A. 10.0 millimols $AlCl_3$ in 1,000 cc.
B. 2.0 millimols Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.58	0	x	.....	...
20	0.56	Slow	xxx	−2.02	7.0
20	0.54	Instant	xxxx	−0.76	6.6
20	0.52	Instant	xxxx	+1.78	5.5
20	0.50	Instant	xxx	+1.90	...
20	0.48	Rapid	xx	+2.00	...
20	0.46	0	x	.....	...
20	0.44	0	x	.....	...
20	0.40	0	x	.....	...
20	0.30	0	x	.....	...
20	0.20	Rapid	xx	+2.16	...
20	0.10	Instant	xxx	+1.84	4.1
20	0.0	Instant	xxxx	+0.76	3.7

Isoelectric mixture:
10.0 millimols $AlCl_3$ in 1,000 cc.
2.0 millimols Na-humate + 26.7 millimols NaOH in 1,500 cc.
pH 6.2.
Al_2O_3 in solution: None.
Humus in solution: None.

Composition of floc: $\frac{0.70 \text{ gm. humus}}{5.0 \text{ millimols } Al_2O_3} = 0.140$ gm. humus per millimol Al_2O_3.

The analysis represents the first isoelectric point. The composition of the floc is expressed in the number of grams of humus per millimol sesquioxide. To express the humus in milliequivalents would be meaningless, for even if we accept the base exchange value as the equivalent, the ratios would be misleading since the humus is quantitatively precipitated whether in combination or not.

In table 50 we have only one isoelectric point within the range covered. But as noted by the migration velocities and by the corresponding curve in

figure 8 a displacement toward a seond isoelectric point is evident. The greater proportion of Al expresses itself in a higher isoelectric pH (5.15) and in a stronger positive charge at lower pH values. There is, however, as yet no tendency to form a stable positive sol.

In table 51a with a proportion of 24 milliequivalents of $AlCl_3$ to 3 of Na-humate the isoelectric pH has climbed to 5.5. On the positive side there is a high maximum charge and then a gradual decline. There is here some tendency to stability as indicated by *XXX* on the positive side.

TABLE 52B

The $FeCl_3$ + Na-humate, system no. 57

A. 10.0 millimols $FeCl_3$ in 1,000 cc.

B. 2.0 millimols Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.58	Slow	x	.....	...
20	0.56	Instant	xxxx	−2.52	6.5
20	0.54	Instant	xxxx	±0.0	5.4
20	0.52	Instant	xxxx	+1.26	4.0
20	0.50	Instant	xxxx	+1.68	3.6
20	0.48	Rapid	xxxx	+2.02	3.3
20	0.46	Slow	xxxx	+2.16	3.2
20	0.40	0	xxxx	+2.16	...
20	0.30	0	xxxx	+1.90	...
20	0.20	0	xxxx	+1.90	...
20	0.10	0	xxxx	+1.68	...
20	0.0	Slow	xxx	+1.60	...

Isoelectric mixture:

10.0 millimols $FeCl_3$ in 1,000 cc.

2.0 millimols Na-humate + 27.0 millimols NaOH in 1,500 cc.

pH 5.4.

Fe_2O_3 in solution: 0.091 millimol.

Humus in solution: None.

Composition of floc: $\frac{0.70 \text{ gm. humus}}{4.909 \text{ millimols } Fe_2O_3} = 0.141$ gm. humus per millimol Fe_2O_3.

In table 51b the porportion of Fe is the same as the proportion of Al in 51a. The same holds for tables 52a and b, and 53a and b. We meet here the same differences in the isoelectric pH values as in the chloridated and sulfated "hydroxides," the "phosphates," and the "silicates" (except the most highly silicated ones). The isoelectric pH of the ferric "humates" is considerably lower than that of the Al-"humates." The comparison can best be shown in figure 8. Table 51b shows some tendency toward stability at very low pH values on the positive side, as seen in the "after mixing" column. The next day the flocculation was, however, "regular," in a single zone. Such differences are due to a "drift" in the charge and in the isoelectric point on standing.

In tables 52a and b, where the proportion is 30 milliequivalents chloride to 2 of humate, the isoelectric pH has increased to 6.2 in the aluminum and to 5.4 in the ferric system. The positive charge reaches a high peak and the aluminum "humate" complex becomes quite stable between the pH values 5.5 and 4.1, giving rise to two zones of flocculation, the so-called "irregular series." After being mixed, the ferric "humate" shows stability below a pH of 3.2, but this is only a transient effect, for the following day the flocculation was continuous.

In tables 53a and b, with a ratio of 30 milliequivalents chloride to 1 of humate, the isoelectric pH is 6.8 for the aluminum and 5.95 for the ferric

TABLE 53A

The $AlCl_3$ + Na-humate, system no. 58

A. 10.0 millimols $AlCl_3$ in 1,000 cc.
B. 1.0 millimol Na-humate in 1,000 cc.

SOLUTION A	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.60	Slow	xxx	−2.00	8.0
20	0.59	Rapid	xxxx	−1.78	7.8
20	0.58	Instant	xxxx	−1.58	7.5
20	0.57	Instant	xxxx	−1.16	7.0
20	0.56	Instant	xxxx	+0.20	6.7
20	0.54	Slow	xxxx	+1.78	5.8
20	0.52	0	x	.....	...
20	0.45	0	0	.....	...
20	0.30	0	0	.....	...
20	0.15	0	0	.....	...
20	0.0	Rapid	xxxx	+0.88	3.7

Isoelectric mixture:
10.0 millimols $AlCl_3$ in 1,000 cc.
1.00 millimol Na-humate + 28.07 millimols NaOH in 1,500 cc.
pH 6.8.
Al_2O_3 in solution: None.
Humus in solution: None

Composition of floc: $\frac{0.35 \text{ gm. humus}}{5.0 \text{ millimols } Al_2O_3} = 0.07$ gm. humus per millimol Al_2O_3.

"humate." The stable zones on the positive side have now become permanent. It is of interest to note that where the stability of the aluminum humate ends, i.e., at pH 3.7, the stable condition of the ferric "humate" just commences. Such differences in behavior, if properly interpreted, must express themselves in the formation of the podzol horizons.

Figure 8 brings out an interesting relationship between the electropositive maxima and the pH. In the case of the aluminum "humates" these maxima coincide with a pH of 4.4 to 4.5 whereas the ferric "humates" attain a maximum positive charge at a pH between 3.2 and a slightly lower value. This

means that the amphoteric sesquioxide constituents attain, as colloids, a maximum electropositive activity at these points, i.e., a maximum electrical neutralizing power (5). Beyond these points, at still lower pH values, the sesquioxide constituent combines with more and more HCl and become undoubtedly more strongly electropositive, but true solution takes place here so rapidly that the total "electropositive quantity" in combination with the negative humus actually decreases, with the result that the complex as a whole becomes less positive.

The pH of the maximum electropositive activity of the sesquioxides will, of course, depend upon the nature of the diffusible anion. The aforementioned

TABLE 53B

The $FeCl_3$ + Na-humate, system no. 59

A. 10.0 millimols $FeCl_3$ in 1,000 cc

B. 1.0 millimol Na-humate in 1,000 cc.

SOLUTION A, 20 cc. + HCl MILLIMOLS	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION: After mixing	FLOCCULATION: Overnight	μ/sec. 1 volt/cm.	pH
0.0	0.60	Slow	xx	.....	...
0.0	0.58	Instant	xxxx	−1.78	6.7
0.0	0.57	Instant	xxxx	−0.92	6.2
0.0	0.56	Instant	xxxx	+1.00	5.7
0.0	0.54	Rapid	xxxx	.....	4.1
0.0	0.52	Slow	xxxx	+2.02	3.7
0.0	0.30	0	0	.....	...
0.0	0.0	0	0	.....	...
0.04	0.0	0	0	.....	...
0.10	0.0	Slow	xxx	+1.26	...
0.40	0.0	Rapid	xxxx	+1.08	...

Isoelectric mixture:

10.0 millimols $FeCl_3$ in 1,000 cc.

1.0 millimol Na-humate + 28.25 millimols NaOH in 1,500 cc.

pH 5.95.

Fe_2O_3 in solution: 0.025.

Humus in solution: None.

Composition of floc: $\frac{0.35 \text{ gm. humus}}{4.975 \text{ millimols } Fe_2O_3} = 0.0704$ gm. humus per millimol Fe_2O_3.

results apply only to the chlorides. The ferric chloride, being more hydrolyzed, requires a higher acidity both for the electrical neutralization and for the positive maximum of the humate complex.

ISOELECTRIC ALUMINUM "PHOSPHO-HUMATE" AND "SILICO-HUMATES"

The natural soil colloid complex being the product of the interaction between a number of different ions it seemed of interest to study the electrokinetic behavior and the composition of the floc of a few, variously composed systems.

Tables 54 and 55 show how the phosphate and the humate ions and the silicate and humate ions compete in combining with the aluminum ion. We must however not lose sight of the OH and the Cl anions, since these are both present and both compete with the others for a place in the complex. Whereas in the preceding systems we were dealing with three different anions we shall here introduce four different anions, counting the humus complex as a single anion.

In order to make the study as comparative as possible, the proportion of $AlCl_3$ to Na_2HPO_4 and to Na_2SiO_3 was taken as in tables 35 and 38a, respec-

TABLE 54

The Al-"phospho-humate," system no. 60

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 5.482 millimols Na_2HPO_4 + 2.0 millimols Na-humate } in 1,000 cc.

SOLUTION A, 20 cc. + HCl MILLIMOLS	SOLUTION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION: After mixing	FLOCCULATION: Overnight	μ/sec. 1 volt/cm.	pH
0.0	0.10	0	x	.....	...
0.0	0.08	Slow	xxx	−1.84	...
0.0	0.06	Instant	xxxx	−0.69	4.4
0.0	0.04	Instant	xxxx	+0.13	3.8
0.0	0.02	Instant	xxxx	+0.48	3.5
0.0	0.0	Rapid	xxxx	+0.41	3.4
0.10	0.0	Rapid	xxxx	+0.18	3.1
0.30	0.0	Rapid	xxxx	+ slight	...
0.50	0.0	Rapid	xxxx	− slight	...

Isoelectric mixture:
5.0 millimols $AlCl_3$ in 1,000 cc.
5.482 millimols Na_2HPO_4
2.0 millimols Na-humate } in 1,500 cc.
2.15 millimols NaOH
pH 3.9.
PO_4 in solution: 1.838 millimols.
Al_2O_3 in solution: 0.088 millimol.
Composition of floc: $Al_2O_3\ (P_2O_5)_{0.742}$
In absence of humus (pH 5.6): $Al_2O_3\ (P_2O_5)_{0.769}$ [see table 35, part III].

tively. In making any comparison it must, however, be remembered that the introduction of the humate modified the pH of the zone of flocculation as well as the isoelectric pH. The latter was, of course, lowered because of the addition of an extra, strongly electronegative component, the humus. The two milliequivalents of Na-humate lowered the isoelectric pH in the phosphated system from 5.6 to 3.9 and in the silicated system from 6.25 to 5.5.

The electronegative effect of the humate is further seen in a recurrence of a maximum in positive charge between pH 3.8 and 3.4 in the phosphated system and between 4.5 and 4.2 in the silicated system. At still lower pH values the phosphated system again becomes isoelectric.

The composition of the isoelectric floc is interesting, for it shows, as might be predicted, that the ions displace one another. The displacement of the PO_4 ion by the "humate" is not very great but it is greater than it appears to be because at a pH of 3.9 the aluminum would, in the absence of the "humate," have combined with considerably more PO_4 than was found in combination in the precipitate, isoelectric at pH 5.6. This is made evident by an extrapolation of the aluminum "phosphate" curve in figure 10. It must be remembered also that there was only 2 milliequivalents of "humate" to 15 of $AlCl_3$

The SiO_3 ion, on the other hand, is strongly displaced by the "humate." From the aluminum "silicate" curve in figure 10, we see that, at a pH of 5.5

TABLE 55

The Al-"silico-humate," system no. 61

A. 5.0 millimols $AlCl_3$ in 1,000 cc.

B. 6.713 millimols Na_2SiO_3 + 2.0 millimols Na-humate } in 1000 cc.

SOLUTION A, 20 cc. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
	cc.				
0.0	20	0		.....	...
0.02	20	Slow	xxx	−1.80	...
0.03	20	Instant	xxxx	−1.38	6.3
0.04	20	Instant	xxxx	−0.56	5.9
0.05	20	Instant	xxxx	+1.00	4.9
0.06	20	Instant	xxxx	+1.26	4.5
0.08	20	Instant	xxxx	+1.60	4.3
0.10	20	Rapid	xxxx	+1.32	4.2
0.20	20	Rapid	xxxx	+1.26	4.1

Isoelectric mixture:
5.0 millimols $AlCl_3$ + 2.18 millimols HCl in 1,000 cc.
6.713 millimols Na_2SiO_3 + 2.0 millimols Na-humate in 1,500 cc.
pH 5.5.
SiO_2 in solution: 4.636 millimols.
Al_2O_3 in solution: trace.
Composition of floc: $Al_2O_3\ (SiO_2)_{0.83}$.
In absence of humus (pH 6.25): $Al_2O_3\ (SiO_2)_{1.63}$ [see table 38a, part III].

there should be about 2.20 mols SiO_2 per mol Al_2O_3 in the isoelectric precipitate. The addition of two millimols of Na-"humate" has reduced the SiO_2 content in the isoelectric precipitate to 0.83 mols per mol Al_2O_3.

This fact is of the greatest significance in relation to the de-silication of the soil complex in the process of podzol formation. That this displacement of SiO_2 by humus takes place in nature is shown by the work of Tamm (7). His figures would, however, have been more valuable from this point of view if the analyses had represented the colloidal fraction separately. The author would like to emphasize the importance and necessity of determining the composition

of the colloidal fraction of soils as represented by the products of hydrolytic decomposition, i.e., the synthetic colloidal complex as distinguished from crystalline fragments (rock flour). For this purpose it would be desirable to work with fractions below 0.2μ in diameter. This is deemed absolutely necessary if we are going to learn anything about the formation and degradation of this complex under natural conditions and about the development of soil horizons. The complete analysis of a soil is of little or no value in a study of this kind. Saturated with sodium most soil colloids will readily disperse to dimensions below 0.2μ and can be separated with the supercentrifuge.

ISOELECTRIC ALUMINUM AND FERRIC "PHOSPHO-SILICATES"

Tables 56a and b and 57a and b show the influence of the PO_4 and SiO_3 ions when present in the same system with $AlCl_3$ and $FeCl_3$.

Since these experiments were not carried out with the same proportions of phosphate and silicate as in the single systems no direct comparison can be made. But the quantities of $AlCl_3$ and $FeCl_3$ were kept at 5 millimols as before. We may therefore compare the composition of these precipitates with the composition—concentration curves in figure 6 (part III) and with the composition—pH curves in figure 10, which represent the single "phosphates" and "silicates."

The comparison brings out that the PO_4 ion causes a very extensive displacement of the silicate ion. We should therefore expect the soil colloidal complex formed from phosphatic rocks to possess a high PO_4 content and to be correspondingly low in SiO_2. A more or less highly phosphated and desilicated complex must also result when phosphatic solutions, as in the leachings from guano beds, react with the products of rock weathering. The PO_4 ion must enter to some extent in all soil colloids since both ground water and sea water contain this ion in small but, if the displacing power is considered, appreciable quantities.

Clarke (2) gives a table of analysis of phosphatic deposits from different parts of the world. The average percentage composition of six samples is as follows: P_2O_5, 39.0; SiO_2, 4.2; Al_2O_3, 20.5; and Fe_2O_3, 6.6. The other constituents are here ignored. In mols P_2O_5 and SiO_2 per mol $Al_2O_3 + Fe_2O_3$ we find the following average composition:

$$R_2O_3 \cdot (P_2O_5)_{1.14} \cdot (SiO_2)_{0.29}$$

which is something of the same order of combination as the aforementioned isoelectric "phospho-silicates."

It would obviously be absurd to express materials of such complex composition in the form of a simple stoichiometric formula, as the mineralogist often delights in doing. When this fails the material is declared "impure." The author would like to ask which part of the complex is to be considered as impurity? From the foregoing it is quite evident that there are any number of

silicated, phosphated, hydroxylated, humated, sulfated,—complexes; a different one in each sample of soil.[2]

Returning to a discussion of the tables we note by a comparison with the curves in figure 6 and 10 that the SiO_3 ion does not displace the PO_4 ion to any apparent degree. In fact if we plot the phosphate content in the floc, and the end concentration as in figure 6, we find that the presence of the silicate has caused more of the PO_4 ions to combine. The same phenomenon was observed by Ghosh (3) who found that a mixture of alumina and silica gel adsorbed a maximum amount of PO_4 from $Ca(H_2PO_4)_2$ when the gel contained 30 per cent SiO_2. This anomaly will be reserved for further discussion in connection with

TABLE 56A

The aluminum "phospho-silicate," system no. 17

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 15.0 millimols Na_2SiO_3 + 10 millimols H_3PO_4 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	9.0	Slow	xxxx	.....	4.4
20	9.2	Instant	xxxx	+0.89	5.2
20	9.4	Instant	xxxx	+0.23	5.5
20	9.6	Instant	xxxx	−0.36	5.7
20	10.0	Instant	xxxx	−0.92	5.9
20	11.0	Opal	xxxx	.....	...

Isoelectric mixture:
5.0 millimols $AlCl_3$ in 1,000 cc.
7.125 millimols Na_2SiO_3 + 4.75 millimols H_3PO_4 in 1,500 cc.
pH 5.6.
SiO_2 in solution: 6.796 millimols.
PO_4 in solution: 0.941 millimol.
Composition of floc: $Al_2O_3\ (SiO_2)_{0.122}\ (P_2O_5)_{0.782}$.

the adsorption of anions and cations by the various isoelectric precipitates at various H-ion concentrations (section VI).

A GRAPHIC REVIEW OF THE ISOELECTRIC PRECIPITATES

Figures 8, 9, and 10 give a graphic representation of the relationship between the electrokinetic behavior, the pH, and the isoelectric composition.

Figure 8 shows the direction and speed of electrical migration of aluminum

[2] In view of this fact the recent announcement of "the origin, nature and isolation of the inorganic base exchange compound in soil" (8) loses in significance, although the announcement has been widely heralded in the press as a discovery of the greatest importance. Any criticism would, however, be premature because thus far only the title of this paper has been published in a scientific journal.

and ferric "humates" at various H-ion concentrations. The figure on each curve indicates the number of grams of humus precipitated with each millimol sesquioxide at the isoelectric point.

Figure 9a shows the electrokinetic behavior at various pH values of: (*a*) aluminum "hydroxide" precipitated from the chloride; isoelectric composition: 0.0048 milliequivalent Cl per millimol Al_2O_3, (*b*) aluminum "hydroxide" from the sulfate; isoelectric composition: 0.0737 millimol SO_4 per millimol Al_2O_3, and (*c*) three aluminum "silicates," isoelectric composition as indicated.

Figure 9b: (*a*) ferric "hydroxide" from ferric chloride; isoelectric composition: 0.0052 milliequivalent Cl per millimol Fe_2O_3, and (*b*) three ferric "silicates;" isoelectric composition as indicated.

TABLE 56B

The ferric "phospho-silicate," system no. 18

A. 5.0 millimols $FeCl_3$ in 1,000 cc.
B. 15.0 millimols Na_2SiO_3 + 10 millimols H_3PO_4 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	8.2	Opal	0	.....	...
20	8.4	Slow	xxxx	+1.44	3.8
20	8.6	Instant	xxxx	+1.21	4.0
20	8.8	Instant	xxxx	+0.64	4.2
20	9.0	Instant	xxxx	− slight	4.6
20	9.2	Instant	xxxx	−0.82	5.0
20	9.4	Rapid	xxxx	.....	...
20	10.0	Opal	0	.....	...

Isoelectric mixture:
5.0 millimols $FeCl_3$ in 1,000 cc.
6.75 millimols Na_2SiO_3 + 4.5 millimols H_3PO_4 in 1,500 cc.
pH 4.2.
SiO_2 in solution: 6.535 millimols.
PO_4 in solution: 0.299 millimol.
Composition of floc: $Fe_2O_3(SiO_2)_{0.087}(P_2O_5)_{0.840}$.

Figure 9c shows the relation between the pH and the charge of three aluminum "phosphates" and one ferric "phosphate" isoelectric composition as indicated. The corresponding tabulations will be found in part III.

Figure 10 shows the relation between the pH and the isoelectric composition of the different precipitates.

THE SESQUIOXIDE-SOIL COLLOID SYSTEMS

The various soil colloids can be isoelectrically flocculated together with the sesquioxides in exactly the same manner as the humus colloid. The reaction of the $AlCl_3$ and $FeCl_3$ with the mineral soil colloids, however, differs quantita-

TABLE 57A

The aluminum "phospho-silicate," system no. 21

A. 5.0 millimols $AlCl_3$ in 1,000 cc.

B. 7.5 millimols Na_2SiO_3
5.114 millimols Na_2HPO_4 } in 1,000 cc.
15.0 millimols NaOH

SOLUTION A	SOLUTION B	FLOCCULATION: After mixing	FLOCCULATION: Overnight	μ/sec. 1 volt/cm.	pH
cc.	*cc.*				
20	6.9	Opal	0	.....	...
20	6.95	Opal	xx	.....	...
20	7.0	Instant	xxxx	+0.82	6.4
20	7.1	Instant	xxxx	±0.0	6.6
20	7.2	Instant	xxxx	−1.21	6.8
20	7.5	Opal	0	.....	...

Isoelectric mixture:
5.0 millimols $AlCl_3$ in 1,000 cc.
2.663 millimols Na_2SiO_3
1.816 millimols Na_2HPO_4 } in 1,500 cc.
5.325 millimols NaOH
pH 6.7.

SiO_2 in solution: 1.747 millimols.

PO_4 in solution: 0.050 millimol.

Composition of floc: $Al_2O_3(SiO_2)_{0.366}(P_2O_5)_{0.353}$.

TABLE 57B

The ferric "phospho-silicate," system no. 22

A. 5.0 millimols $FeCl_3$ in 1,000 cc.

B. 7.5 millimols Na_2SiO_3
5.114 millimols Na_2HPO_4 } in 1,000 cc.
15.0 millimols NaOH

SOLUTION A	SOLUTION B	FLOCCULATION: After mixing	FLOCCULATION: Overnight	μ/sec. 1 volt/cm.	pH
cc.	*cc.*				
20	6.7	Opal	xx	.....	...
20	6.8	Instant	xxxx	+1.68	4.8
20	6.9	Instant	xxxx	−0.95	6.2
20	7.0	Instant	xxxx	−1.78	6.45
20	7.1	Rapid	xxxx	−2.02	6.65
20	7.2	Opal	0	.....	....

Isoelectric mixture:
5.0 millimols $FeCl_3$ in 1,000 cc.
2.576 millimols Na_2SiO_3
1.766 millimols Na_2HPO_4 } in 1,500 cc.
5.152 millimols NaOH
pH 6.4.

SiO_2 in solution: 2.012 millimols.

PO_4 in solution: 0.045 millimol.

Composition of floc: $Fe_2O_3(SiO_2)_{0.228}(P_2O_5)_{0.344}$.

tively from the reaction of these compounds with the humus complex, and the various mineral soil colloids show great quantitative differences among themselves. The combining power of the humus with bases is, as already stated, much greater than that of the mineral soil complex, even when the latter is highly silicated. The humus is therefore more highly electronegative and requires more of an electropositive component for electrical neutralization.

The mineral soil complexes vary greatly in "electronegativity" depending upon the degree to which they are silicated or, more generally, upon the degree

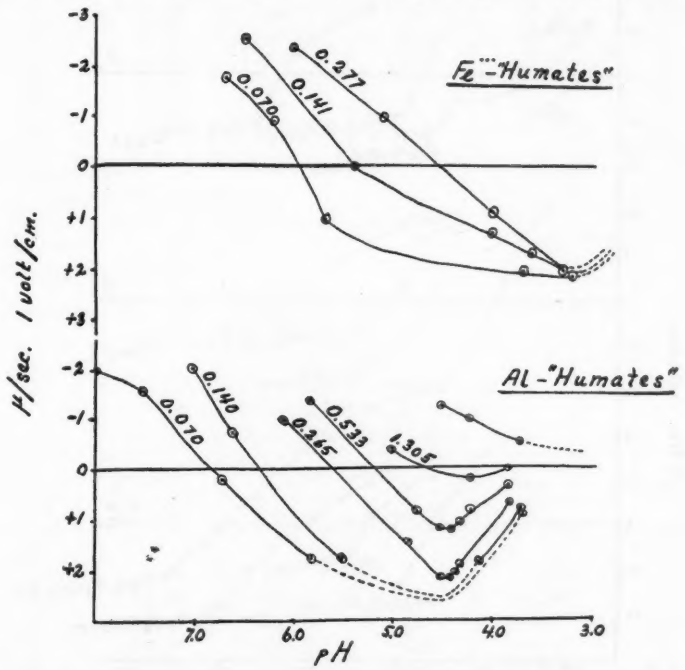

FIG. 8. THE RELATION BETWEEN THE pH, THE SIGN OF CHARGE, THE MIGRATION VELOCITY, AND THE RATIO OF GRAM HUMUS TO MILLIMOL SESQUIOXIDE IN A SERIES OF ALUMINUM AND FERRIC "HUMATES".

to which acid radicals exist in (partial) combination in the insoluble alumino or ferric complex. If highly silicated, the soil complex will precipitate isoelectrically, at a given pH, with a much greater porportion of sesquioxide than if it is only slightly silicated. The highly silicated complexes are not by themselves amphoteric but require, like the humus complex, a definite proportion of sesquioxide to form an amphoteric complex. With the minimum quantity of sesquioxide the isoelectric pH is low, but becomes progressively higher as the proportion of sesquioxide is increased, just as in the case of the humus complex. Soil

complexes of a low silication, e.g., a silica/sesquioxide ratio below 2.0, are by themselves amphoteric and any introduction of additional sesquioxide will only result in a higher isoelectric pH.

In order to show the general behavior of the sesquioxide-soil colloid systems, and for future reference in connection with the laws governing ion adsorption

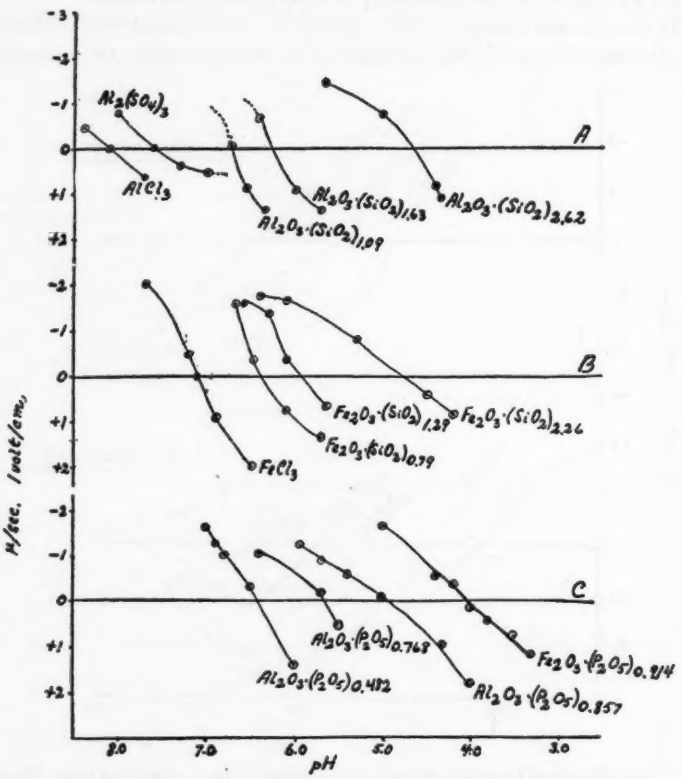

FIG. 9. THE RELATION BETWEEN THE pH, THE SIGN OF CHARGE, AND THE MIGRATION VELOCITIES OF "HYDROXIDES," "SILICATES," AND "PHOSPHATES" OF ALUMINUM AND IRON

The "silicate" and "phosphate" formulas refer to the isoelectric composition.

and exhange, table 58a and b are here appended. Bentonite was selected because of its strong electronegative character and high cation exchange capacity. One millimol sesquioxide was precipitated with 0.5 gm. bentonite, the isoelectric pH being 6.75 in the $AlCl_3$ system and 6.5 in the $FeCl_3$ system. Comparing this to the figures in table 50 were the proportion of humus is nearly the same (0.533 gm. per millimol Al_2O_3) we see that the "humated" sesquioxide

TABLE 58A

The $AlCl_3$ + bentonite, system no. 101

A. 4.0 millimols $AlCl_3$ in 1,000 cc.

B. 1.0 gm. bentonite in 1,000 cc.

SOLUTION A	SUSPENSION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.28	0	x	−2.44	...
20	0.27	Rapid	xx	−1.96	...
20	0.25	Instant	xxxx	−1.54	7.8
20	0.24	Instant	xxxx	−1.33	7.3
20	0.23	Instant	xxxx	−0.38	6.85
20	0.22	Instant	xxxx	+0.40	6.6
20	0.21	Instant	xxxx	+1.01	6.3
20	0.20	Slow	xxxx	+2.04	5.8
20	0.18	0	x	+2.10	4.6
20	0.16	0	x	+2.03	4.4
20	0.10	Slow	xxxx	+1.79	4.2

Isoelectric mixture:

4.0 millimols $AlCl_3$ in 1,000 cc.

1.0 gm. bentonite + 11.75 millimols NaOH in 1,500 cc.

pH 6.75.

Al_2O_3 in solution: None.

Composition of floc: $\frac{\text{1 gm. bentonite}}{\text{2 millimols } Al_2O_3}$ = 0.5 gm. bentonite per millimol Al_2O_3.

TABLE 58B

The $FeCl_3$ + bentonite, system no. 102

A. 4.0 millimols $FeCl_3$ in 1,000 cc.

B. 1.0 gm. bentonite in 1,000 cc.

SOLUTION A	SUSPENSION B, 20 cc. + NaOH MILLIMOLS	FLOCCULATION:		μ/sec. 1 volt/cm.	pH
		After mixing	Overnight		
cc.					
20	0.28	0	x	−2.34	...
20	0.27	Slow	xx	−2.10	...
20	0.26	Rapid	xxx	−1.90	8.0
20	0.25	Instant	xxxx	−1.60	7.3
20	0.24	Instant	xxxx	−1.02	6.9
20	0.23	Instant	xxxx	±0.0	6.5
20	0.22	Instant	xxxx	+1.05	5.95
20	0.21	Instant	xxxx	+1.79	5.4
20	0.20	Rapid	xxx	+2.06	4.1
20	0.18	Slow	xx	+2.16	3.7
20	0.16	Slow	x	+2.18	3.2
20	0.10	Rapid	xx	+1.96	...

Isoelectric mixture:

4.0 millimols $FeCl_3$ in 1,000 cc.

1.0 gm. bentonite + 11.5 millimols NaOH in 1,500 cc.

pH 6.5.

Fe_2O_3 in solution: None.

Composition of floc: $\frac{\text{1 gm. bentonite}}{\text{2 millimols } Fe_2O_3}$ = 0.5 gm. bentonite per millimol Fe_2O_3.

has a much lower isoelectric pH (5.15) than the "bentonated" sesquioxide. At the same pH the quantity of bentonite electrically neutralized by the aluminum would be very much greater than the quantity of humus so neutralized. The quantities would doubtless be in inverse proportion to the cation exchange capacity.

We have employed the terms "silicates," and "humates," keeping in mind that the colloidal complex does not represent a combination of any one pair of

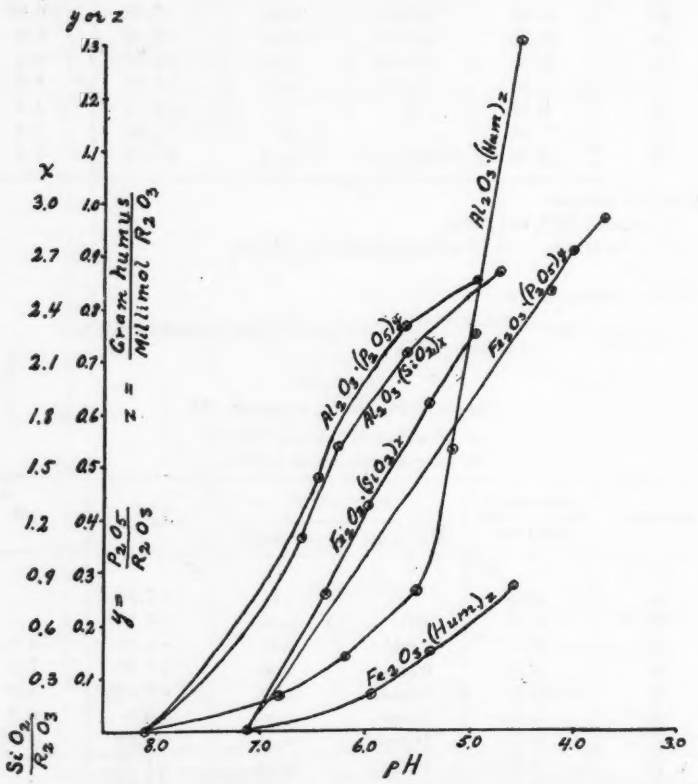

FIG. 10. THE RELATION BETWEEN THE pH AND THE ISOELECTRIC COMPOSITION OF ALUMINUM AND FERRIC "PHOSPHATES," "SILICATES," AND "HUMATES"

ions alone. The reaction between bentonite and the salts of aluminum and iron is apparently of the same nature as the reaction of these salts with the silicate and humate of sodium. The bentonite plays the part of the acid radical, but it would obviously be meaningless to call the resulting complexes "bentonates." There can be no doubt that the Al and Fe valences partly interact with the free silicate valences in the bentonite. The new complex repre-

sents then a less silicated complex than that of the original bentonite. This will be brought out in the studies on ion adsorption and exchange.

SUMMARY

This, the second paper, on isoelectric precipitates, deals with the "humates," "phospho-humates," "silico-humates," and "phospho-cilicates" of aluminum and iron.

The "humates" differ from the "silicates" and "phosphates" in that the colloidal humic complex is quantitatively precipitated by the $AlCl_3$ and $FeCl_3$, in showing an electropositive maximum on the acid side of the isoelectric point and, where the proportion of humus is high, in having a second isoelectric point.

The ferric "humates" are isoelectric at a much lower pH than the aluminum "humates" of corresponding composition.

The humate ion, or ion complex, displaces the PO_4 ion and, to a still greater extent, the SiO_3 ion. The PO_4 ion strongly displaces the SiO_3 ion. There is no apparent displacement of the PO_4 ion by the SiO_3 ion, for in the presence of the latter the proportion of the P_2O_5 in the complex increases somewhat. This anomaly may be due to the formation of an addition complex and will be discussed later in connection with ion adsorption and exchange.

The mineral soil colloid complexes react with aluminum and iron, forming isoelectric precipitates in exactly the same manner as the humus complex.

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BOOK REVIEWS

Grundzüge der Bodenkunde. By FRIEDRICH SCHUCHT. Paul Parey, Berlin, 1930. Pp. VII + 405, figs. 135.

The author, who is director of the Institute of Geology, Mineralogy, and Soils of the University of Berlin, notes that the data of soil science are of interest not only to students of agriculture and forestry, but also to those of geology, botany, and economic geography. The author wrote his book with this in mind.

The major divisions of the book include soils and soil science, soil formation, soil physics, the chemistry of soils, the biology of soils, influence of climate on soil formation, the soil as a culture medium for plants, soil classification and mapping, the soils of Germany, and methods of soil examination.

The author's style is clear and the discussion is usually compact. Despite the briefness of the treatment made necessary by the character of the book, the discussion of the various topics is usually effective. For example, the author's description of the formation of lateritic soils, of peat soils and their formation, of base exchange and soil acidity, is quite satisfactory. There is also a lucid discussion of climate in its relation to soil formation. The portion dealing with the soils of Germany will be of particular interests to teachers located in other countries. The bibliography is arranged under various topics and is quite adequate for a book of this character.

Die Bedingungen der Wirtschaftlichkeit der Handelsdüngemittel. By L. VON KREYBIG. Paul Parey, Berlin, 1930. Pp. 128, figs. 5, colorplate 1.

The book is dedicated to Prof. F. Löhnis, of the University of Leipsic, and contains a foreword by him.

The topics dealt with in the book include chemical factors which influence the action of fertilizers; the influence of microörganisms on the action of manures and fertilizers; the plant physiological factors affecting the action of fertilizers; conditions relating to the application and economic returns from nitrogenous fertilizers, phosphates, potash fertilizers, and mixed fertilizers; and practical considerations in the use of fertilizers.

The author develops some interesting points of view concerning the plant-food resources of the soil, the supplementing of these with plant-food derived from animal manures and chemical fertilizers, the significance of microörganisms in the circulation of plant-food, and the economic considerations that enter into the utilization of the plant-food resources derived from within or without the soil.

Manual of Bacterial Plant Pathogens. By CHARLOTTE ELLIOTT. The Williams and Wilkins Company, Baltimore, Md., 1930. Pp. IX + 349.

The author, who is associate pathologist in the Bureau of Plant Industry, U. S. Department of Agriculture, has arranged her treatise in four major divisions; namely, Alphabetical List of Plant Pathogens, Alphabetical List of Non-Pathogenic Organisms Associated with Plant Disease, Chronological Chart of Plant Pathogens, and Index of Host Plants and Bacteria.

The individual species of plant pathogens are described in the first section, in each case the name of the organism, synonymous name, symptoms, host plant, geographical distribution, and literature are recorded. This portion of the book occupies 270 pages out of a total of 349. A similar treatment is accorded to non-pathogenic organisms associated with plant diseases (p. 273–317). The chronological charts of plant pathogens (p. 320–331) offer convenient reference material. The book will undoubtedly be appreciated not only by plant pathologist, but also by botanists generally, microbiologists, and horticulturists.

Mycorrhiza. By M. C. RAYNER. Wheldon & Wesley, Ltd., London, 1927. Pp. VI + 246, figs. 64.

The increasing interest in soil biology has served to attract a greater degree of attention to mycorrhiza. Much has been published on the subject, but, unfortunately, the material is scattered in various journals and reports and not always readily accessible to the student. For this reason, the author has rendered a helpful service in having brought together much of the scattered material. She has organized the data and has presented them in a very readable way. As has been noted by the author:

> The mycorrhiza habit first attracted attention as a characteristic of woodland soils. Modern experimental research has once more focused attention on the significance of this fact and emphasized the importance of mycorrhiza as a biologic soil factor affecting the vegetation of woodlands in common with that of other types of humus soil. The practical application of the newer knowledge to natural conditions has already attracted the attention of foresters, thus opening up a new and fascinating field of research, promising alike to the botanist, the forester and the student of soil science.

The book is divided into three parts, dealing, respectively, with the early period (1840-1880), the second period (1880 to about 1900), and the modern period (1900–1925). There are, in all, 11 chapters. These deal with the various hypotheses and controversies that have centered about the subject of mycorrhiza. The reader will find among the multitude of topics discussed: the Monotropa controversy, De Bary's theory of symbiosis; the morphological studies on mycorrhiza by Frank; Hartig's theory of parasitism; the contributions of various workers on the subject of saprophytes and hemisaprophytes; the cytology of intracellular digestion; and autotrophic and mycotrophic plants. There is a discussion of mycorrhiza of Arctic and Alpine plants; of orchidaceae; ericaceae; endotrophic and ectotrophic mycorrhiza; "mycorrhiza"

in bryophyta; tuberisation; and the physiological significance of mycorrhiza and the nutrition of mycorrhiza plants. A very satisfactory bibliography has been supplied by the author.

Handbuch der Bodenlehre, volume II. Edited by E. BLANCK. Julius Springer, Berlin, 1929. Pp. VI + 314, figs. 50.

The first volume of the Handbuch (reviewed on page 260, volume XVIII of SOIL SCIENCE) deals with the scientific principles relating to the origin of soils. The second volume deals with the weathering of rocks and the climatological processes of weathering. The contributors to the first volume, aside from the editor, include Fesefeldt, Giesecke, Hager, Heide, Meigen, Passarge, Philipp, Rehorst, and Rüger. The contributors to the second volume include, aside from the editor, Knoch, Rehorst, Schellenberg, Schubert, and Wasmund.

The principal divisions of the book deal with factors of climate and climate zones; the climate of the soil surface and of the lower portion of the atmosphere in Central Europe; variation in climate in recent geological periods; pollen studies as a means of measuring climatological factors of recent geological periods and of the age of humus formations; general facts about weathering; physical factors of weathering; chemical factors of weathering; the decomposition of organic substances; biological weathering due to living organisms; and biological weathering as influenced by organic substances undergoing decomposition.

The present volume contains important contributions to our knowledge of climate as a major factor in the genesis and evolution of soils. The extensive bibliography is both suggestive and helpful, and should enable the student of soils, as well as the ecologist and plant physiologist, to understand more clearly the influences that have played a part in the past, as they now do, in maintaining dynamic conditions in the soil.

Klima und Boden in ihrer Wirkung auf des Pflanzenleben, second edition. By HENRIK LUNDEGÅRDH. Gustav Fischer, Jena, 1930. Pp. x + 480, figs. 129, maps 2.

There is an evident tendency among workers in the fields of plant and soil science to organize the pertinent facts in such fashion as to permit of more sound and effective generalizations. The present volume is a good illustration of this tendency. This treatise on climate and soil in their relation to plant life is the result of the author's painstaking study in various fields. As he himself expresses it:

> The field of experimental ecology, new and yet rapidly expanding, is criss-crossed with so many paths of research and so many trends of thought that its description, if it is not to exceed certain limits, must confine itself to essentials only. I have tried to extract much from the most recent literature on the subject. Nevertheless, I have considered it desirable to lay emphasis on those parts that are related to my own experimental inquiries.

A brief historical discussion is followed by chapters on the light factor, the temperature factor, and the water factor. Other chapters deal with the soil, its formation and general ecological properties, the physical nature and the aeration of soils, the chemical soil factors, soil microörganisms, the carbonic acid factor, and the more important principles which relate to experimental ecology.

The author is to be commended for the logical arrangement and discussion of the various topics, the helpful footnotes, the rather satisfactory bibliography, and the carefully prepared index. The publishers deserve credit for the attractive appearance of the book.

Bacteriology, second edition. By STANLEY THOMAS. McGraw-Hill Book Company, Inc., New York, 1930. Pp. XV + 301, figs. 38.

The author, who is professor of bacteriology at Lehigh University, has written a textbook which attempts to outline in a balanced way the more important fields of general bacteriology. In the introduction to the first edition, which was published in 1925, he noted that

> While medical bacteriology has been of invaluable service to mankind, and while there is no doubt that the impetus given by Pasteur, Koch and Lister has put this branch of the science ahead of the other branches in pure achievement, the fact must not be lost sight of that medical bacteriology is simply one branch of a science which is, like its parent sciences chemistry and biology, of educational and practical value to mankind in many and varied fields of endeavor.

In the second edition, which was revised and rewritten, he says:

> Modifications, additions and omissions have been required in every chapter, and in most cases an entirely new method of presentation has been employed.

The book contains 17 chapters, which deal with such topics as the history of bacteriology; classifications; morphology, physiology, and cultivation of bacteria. There is also a discussion of bacterial enzymes and of microörganisms other than bacteria. Special chapters are devoted to bacteria in the soil, water, sewage, air, and foods. Three chapters are devoted to a discussion, respectively, of pathogenic bacteria, immunity, and hygiene and sanitation. The last chapter deals with bacteria in industry. The frontispiece is a good reproduction of one of Pasteur's protraits.

Ergebnisse der Agrikulturchemie, volume I. Edited by F. HONCAMP. Verlag Chemie, Berlin, 1929. Pp. VII + 281, figs. 28.

This volume was prepared at the request of the section on agricultural chemistry of the Association of German Chemists, and represents contributions from men well known among the chemists of Germany and of other countries. The introductory chapter, entitled "Chemistry and Agriculture," was written by Prof. A. Binz, of Berlin. The titles of the other chapters and the names of their authors follow: "Distribution and Circulation of Iodine from the Point of

View of its Significance in Soils," by Griessbach; "The Significance of Iodine in Plant Nutrition," by Ströbele; "The Iodine Problem in Animal Nutrition," by Scharrer; "The Combined Action of the Elements Potassium and Sodium in Plant Growth," by Maiwald; "The Cultivation and Manuring of Soils," by Alten; "Modern Chemical and Biological Points of View in the Treatment of Stable Manure," by Ruschmann; "Definite Relations in the Assimilation of Protein," by Wöhlbier; "Experiences, Practical Observations and Results Relating to Phosphoric Acid Studies in Soils," by Doerell; "The Lime Resources of our Soils," by Behrens; "On the Determination of the Saturation Point of Soil in Accordance with Newer Methods," by Kappen; "Electrodialysis and the Problem of Mineral Soil Acidity," by Trénel; "The Measurement of Soil Reaction, the Influences Modifying Soil Reaction and the Biological Appraisal of the Soil," by Görbing and Adolphi; "Results Obtained in Determining the Lime Requirements and in Modifying the Saturation Point of Soils," by Pfeil.

The book contains no index, but it is to be presumed that a general index will be included in the last volume of the series.

Soil. By ARCHER BUTLER HULBERT. Yale University Press, New Haven, 1930. Pp. 227, figs. 7.

The title of the book is somewhat misleading in that the term "soil" is used, in part at least, as being equivalent to the term "land."

In writing the book, the author had a definite objective, as is indicated in the preface. He says:

> The main theme of the present volume is the quite ignored one of the influences of the soil on American settlement and expansion. The plan of the volume, however, has been arranged in the hope of doing more than presenting merely a new and important phase of American history; it is offered as a kind of non-classroom textbook for those who may some day undertake to produce the constructive type of local history so greatly needed.

The author states further that he has tried to show "how geological, climatic, hydrographic and edaphic factors have been and may be used to clarify history, particularly the history of American occupation and expansion."

The 21 chapters deal with the basis of provinces; climatic influences on man and vegetation; the waterway keys to our soil provinces; some aspects of river control; highland pathways of conquest and migration; the story of our soils; soil and migration; the meadows of New England; the call of the Connecticut; the Nipmuck and chestnut countries; the tidewater pioneers; the Virginia Piedmont; human seed on stony ground; Penn's forest empire; Scot and Celt on the American frontier; the grand advance; beyond the Shenandoah; the conquest of the Alleghenies; the blue grass region of Kentucky and beyond; types of soil influence in the west. There is also an appendix entitled "A New Basis for the Study of Local History."

Those interested in the field of soil science, as well as economists, sociologists, and historians will find much that is suggestive and helpful in this book.

Lehrbuch der allgemeinen Bodenkunde. By ALEXANDER STEBUTT. Gebrüder Borntraeger, Berlin, 1930. Pp. XII + 518, figs. 55.

Formerly connected with soil research activities at Saratov and Moscow and now professor at the University of Belgrad in Jugoslavia, the author is intimately acquainted with the accomplishments of the Russian school of soil science. He has had also wide experience as a teacher of soils, and possesses, for this reason, a broad outlook on the whole field of soil science. In planning the book he was guided by the central thought that is clearly expressed in the preface. He says:

> Any field of science may attain unity only when its parts are tied together by a central, leading thought. This leading idea is brought to us by Soil Science in its new conception of the soil as a natural body *suis generis* whose condition is a dynamic one. Thanks to this dynamic condition, the soil is passing through the process of development and evolution as opposed to the fundamental idea in the old conception of the soil as a dead, mechanical accumulation of rock fragments and devoid of energy. This book represents the systematic development and expression of the central thought and reflects essentially, the conception of the soil as a dynamic system.

The first part of the book, entitled "The Soil Forming Substratum," contains chapters on the composition of the earth's crust, formation of klastic sediments, the porous soil mass as a disperse system, colloidal systems, soil porosity, and the relation of soils to water, air, organic substances, and heat.

The second part deals with the dynamics of soils and contains chapters on the significance of water in soil formation processes, the decomposition of minerals, the synthesis of soil compounds, soil acidity, mobility of soil constituents, impoverishment of soil layers, and enrichment of soil layers.

In the third part, the general topic of the "genesis of soils," is considered in connection with the more important changes that occur in soil formation, zones of the earth's surface and their relation to one another, plant societies and soils, variations in soil forming processes in different zones, and soil classes from the points of view of immaturity, zeolite formation, degradation.

The fourth part deals with soil fertility as the applied phase of soil science.

JACOB G. LIPMAN.